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JOURNAL OF CHEMICAL EDUCATION

for October, 1937

OFFICIAL MONTHLY PUBLICATION OF THE DIVISION OF CHEMICAL EDUCATION OF THE AMERICAN CHEMICAL SOCIETY

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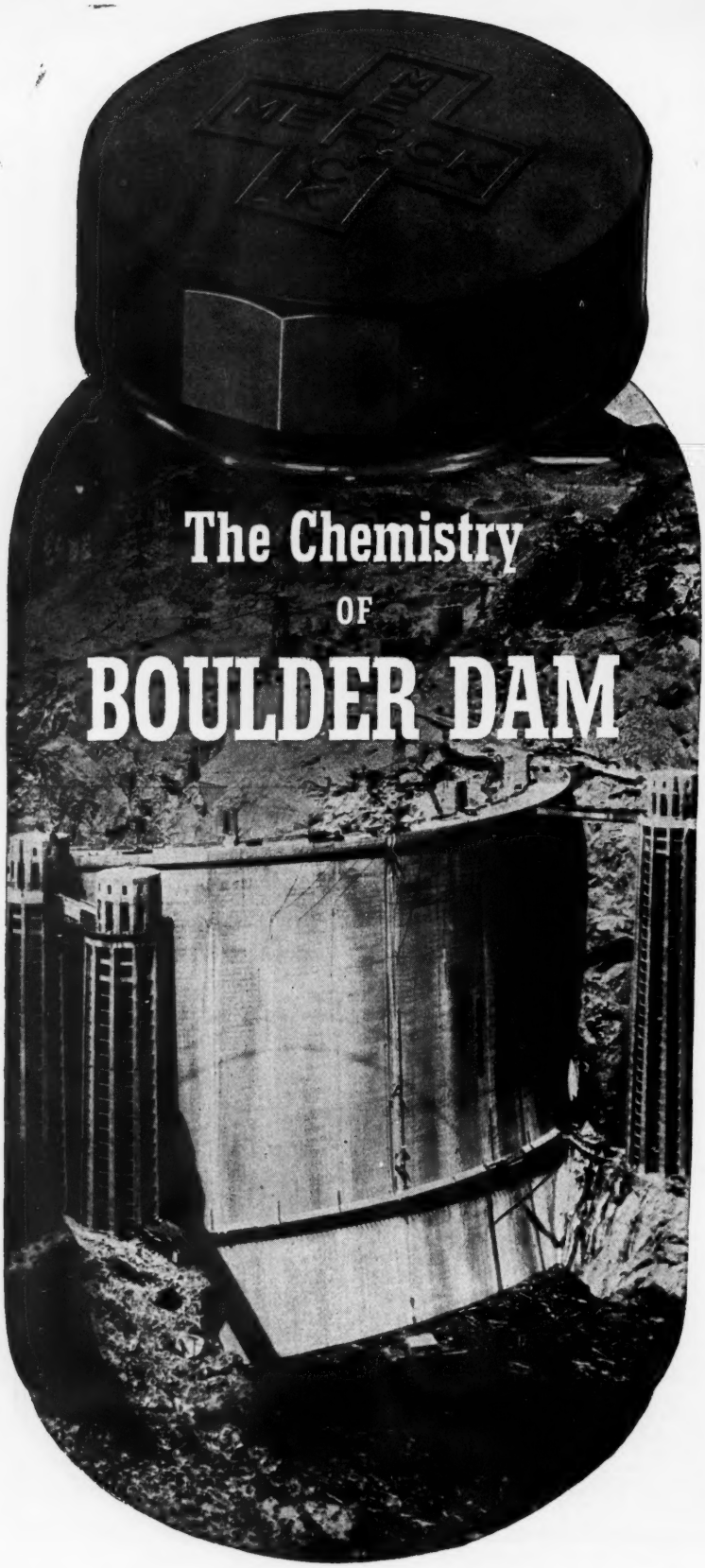

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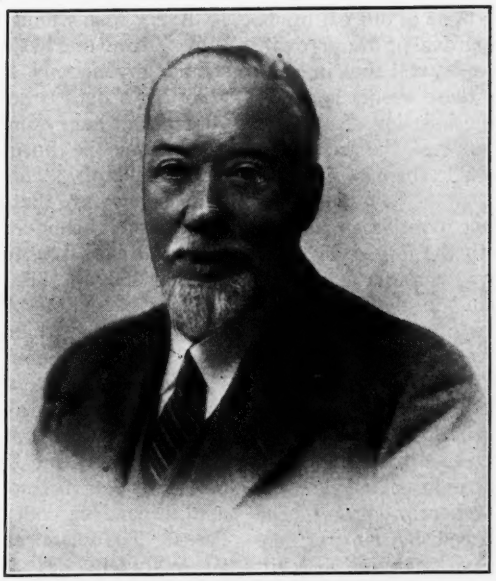

J. J. VAN LAAR (1860–)

For biographical note contributed by Dr. H. S. van Klooster, of Rensselaer Polytechnic Institute, see page 459. Dr. van Klooster also lent the photograph here reproduced.

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EDITOR'S OUTLOOK

"GOD HELPS THOSE THAT HELP THEMSELVES." It is a delightful and ever-fresh surprise to us to learn that someone has read one of our editorials and has been moved, either by approval or disapproval, to the extent of expending ink, paper, and time in comment thereon. Our pleasure in these events is somewhat tempered, however, and the inflation of our ego is considerably abated by evidence of the frequency with which we manage to mishandle the exposition of our own ideas.

Some of our friends saw in last month's emanation a perilous editorial excursion into the foreign fields of political and social controversy. Another conceives our attitude to be "un-Christian" in that we would apply to human affairs the "law of the jungle," and "un-American" in that we deny certain "God-given rights" guaranteed by the Constitution. Actually, our little dissertation was intended as a realistic lay sermon on the text, "Faith without works is dead."

All human beings are given to day-dreaming. The dreams of the realistic and the industrious take the form of plans for future achievement. Those of the muddle-headed, the lazy, and the dishonest are mere orgies of wishful musing; they evaporate in the vociferous assertion of "God-given rights" to goods or privileges that do not in fact exist save in the mind of the dreamer, and that can be created and safeguarded only by human intelligence, energy, and resolution. The great mass of human mediocrity never seems to grasp the truth that rights cannot be created by mere assertion, any more than wealth can be created by printing presses. The makers of our Constitution, like all reasonably sensible men, realized that in asserting certain human rights they were only giving expression to an ideal—an ideal that they must take definite steps to realize and to secure. The average man (which is to say, the fool) having claimed a "right," and finding that actually he has it not, develops a persecution complex, invents personal devils, and runs after quacks of one description or another.

It is, of course, only incidental that confidence men fatten on human folly, and that politicians, being for the most part confidence men of the first and dirtiest water, exploit this particular folly to the limit.

"Every man willing to work has the right to a job." Why? If no one has need of the services he offers, why should anyone buy them? Nobody claims that our tailor has a right to sell us a suit whether we want it or not. Smart buggy and wagon manufacturers went into the automobile business; others went to the wall; some did both. The working man seldom seems to divine, however, that if the services he offers are not in demand it behooves him to think of other services to offer. He has a right to a job, to public charity, or else—.

What has all this to do with chemical education? Perhaps a true story we recently told a discouraged and self-pitying young instructor will serve to make the connection clearer.

A young associate took up his first teaching position at a small state university. He found in the way of equipment a water pump just capable of operating a Büchner filter, one blast lamp equipped with a foot bellows, a few thermometers of doubtful accuracy, and a miscellaneous collection of test-tubes, beakers, and flasks. The chemical stock was insufficient to put a single student—let alone a class—through a course of Emil Fischer's preps. The chemical library was nonexistent.

He began his research in a library to which he could make occasional half-day and holiday trips by trolley. The compilation he turned out is still the standard reference in the field. He made outside contacts and took on consulting work, obtaining in return appropriations for much-needed equipment and extra supplies. He squeezed every nickel's worth of value out of the meager budget allowed him. Gradually he accumulated a reference shelf in one corner of his laboratory. Eventually he began to turn out chemical papers that merited and received general respect. In a few years he made what had seemed a dead-end job into one that many another young fellow would have been glad to get. Subsequently he was called to a better position. Now many of his students think he is "sitting pretty" and wish their prospects were as bright.

The METAL CARBONYLS*

I. HISTORY II. PREPARATION

WM. E. TROUT, JR.

Mary Baldwin College, Staunton, Virginia

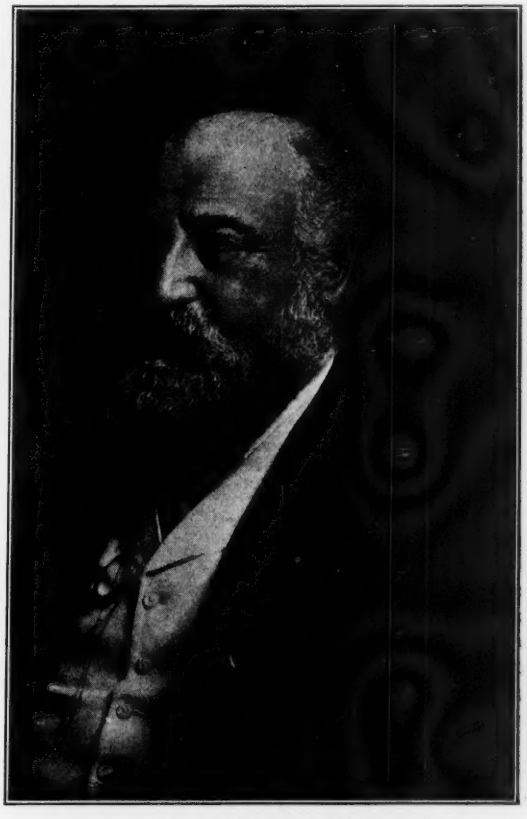
NOT HALF a century has elapsed since the discovery of nickel carbonyl, the first recognized member of a class of peculiar compounds known as the metal carbonyls. Since 1890 an interesting and growing body of literature has been published concerning these compounds, and the developments have been partially summarized in a number of places (*1*). However, a general survey of this interesting chapter of chemistry is not readily available to the student, and this lack has prompted the writing of the present article.

I. HISTORY

Although nickel carbonyl was the first of the compounds now known as the metal carbonyls to be discovered, mention should be made of an earlier known compound which often receives the name of "potassium carbonyl," and which may be confused with the true metal carbonyls. As early as 1834, fifty-six years before the discovery of nickel carbonyl, Justus von Liebig (*2*) passed carbon monoxide over molten potassium and obtained a compound which could be represented by the empirical formula, KCO. This compound received the name, "Kohlenoxidkalium," which may be translated as "potassium carbon oxide." This compound has acquired special significance in connection with the manufacture of potassium by reduction of potash with carbon, where the formation and subsequent violent decomposition of potassium carbonyl has been considered for many years as the cause of occasional damaging explosions. Although itself the subject of controversy arising from conflicting evidence, the reputed instability of potassium carbonyl as well as its empirical formula, KCO, both suggest a relationship of this compound to the relatively unstable metal carbonyls. However, the compound has been thoroughly studied and has been shown, particularly by Nietski and Benckiser (*3*), to be identical with the potassium salt of an organic compound, hexahydroxybenzene, which may be represented by the graphic formula

As we shall see, this formula indicates a structure different from that generally assigned to the true metal carbonyls.

It was not until 1890 that Ludwig Mond, with his coworkers, Carl Langer and Friedrich Quincke (*4*), announced the discovery of nickel carbonyl, $Ni(CO)_4$, the



Courtesy of Mr. H. J. Pooley, General Secretary, Society of Chemical Industry

LUDWIG MOND
1839–1909

Born in Cassel, Germany, Mond held positions in several chemical firms before going to England at the age of 23. He introduced the Solvay process into England, and founded an alkali factory which has been called the largest in the world. Mond discovered the first metal carbonyl and made important contributions in this field. He held a number of important offices, including the presidency of the Society of Chemical Industry in 1888.

* This is the first of a series of four articles concerning the metal carbonyls. The author reserves all rights to these articles.

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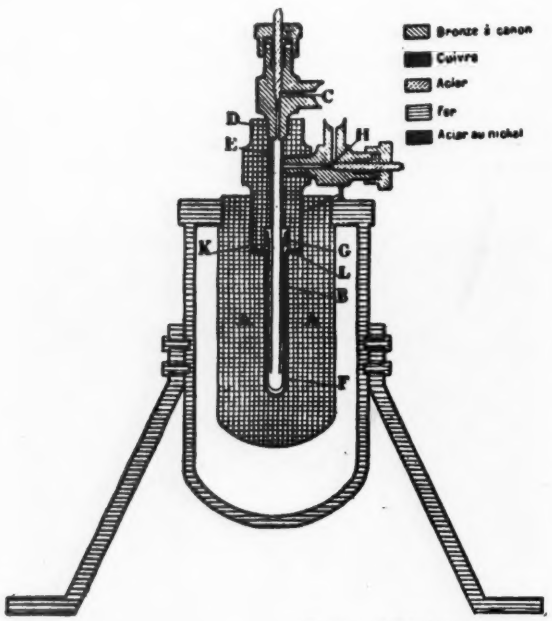
first of a series of related compounds of metal and carbon monoxide. A detailed account of this discovery was interestingly related by Ludwig Mond (*5*) before the New York Section of the Society of Chemical Industry at the November meeting in 1895. The firm of Brunner, Mond and Company was endeavoring to prepare chlorine from ammonium chloride, which, in turn, was obtained as a by-product of the ammonia-soda proc-



Courtesy of Chimie & Industrie

FIGURE 1.—THE FURNACE USED BY MOND AND HIS COLLABORATORS IN THE PREPARATION OF METAL CARBONYLS AT HIGH TEMPERATURES UNDER HIGH PRESSURES

ess, widely known as the Solvay process. This attempt to make the ammonia-soda process more economical was undertaken as a measure of preparedness in the event that the LeBlanc process would be used to produce sodium carbonate as a by-product of the bleaching powder industry, and would thus become a dangerous rival.

One of the obstacles retarding the successful production of chlorine proved to be the unusually rapid corrosion of the nickel valves on the brick-lined tanks in which ammonium chloride was vaporized. Attempts to study this corrosion in the laboratory proved that it resulted from the action of a small amount of carbon monoxide present in the carbon dioxide used to sweep ammonia from the vaporizing tanks. It was found that the carbon monoxide was partially converted into carbon dioxide, and a black mixture of nickel and amorphous carbon was deposited. This observation led to a more elaborate study of the reaction of carbon monoxide with finely divided nickel.

"In the course of these experiments finely-divided nickel, formed by reducing nickel oxide at 400° by hydrogen, was treated with pure CO in a glass tube, at varying temperatures, for a number of days, and was then cooled down in a current of CO before it was removed from the tube. In order to keep the poisonous CO out of the atmosphere of the laboratory, we simply lit the gas escaping from the apparatus. To our surprise we found that, while the apparatus was cooling down, the flame of the escaping gas became luminous and increased in luminosity as the temperature got below 100°C. On a cold plate of porcelain put into this luminous flame, metallic spots were deposited similar to the spots of arsenic obtained with a Marsh apparatus; and on heating the tube through which the gas was escaping we obtained a metallic mirror, while the luminosity disappeared"(*5*).

It was discovered that the issuing gas contained a substance which could be condensed to a colorless liquid with a musty odor and with remarkably high refractive index and cöefficient of expansion—a compound corresponding to the formula $Ni(CO)_4$.

The unusual nature of the compound immediately attracted the attention of such investigators as Marcellin Berthelot, Sir James Dewar, H. O. Jones, Alwyn Mittasch, and others, who rapidly advanced our knowledge concerning nickel carbonyl. Ludwig Mond was amply rewarded when his presumably purely academic discovery provided a means of separating nickel from cobalt by the familiar Mond Process. By 1895, nickel from Canadian matte was being refined in an experimental plant in London at the rate of one and one-half tons weekly.

But we must return to 1890. Encouraged by their success in preparing nickel carbonyl Mond and his coworkers immediately attempted to prepare carbonyls from all the metals at their disposal. However, it was Marcellin Berthelot (*6*) who first announced the formation of a volatile compound of carbon monoxide and iron on June 15, 1891. Fourteen days later, on June 29, 1891, Mond and Quincke (*7*) disclosed their independent discovery of a volatile iron carbonyl. Although the formula which they published at the time was incorrect, later in the year Mond and Langer (*8*) announced the compound to be the liquid iron pentacarbonyl, $Fe(CO)_5$. By subjecting this compound to the action of light, they obtained iron enneacarbonyl, $Fe_2(CO)_9$. However, Mond and Quincke did not discover the nature of this compound at the time. It was Dewar and Jones (*9*) who determined its nature and also discovered a third carbonyl of iron, iron tetracarbonyl, which has been shown to have the formula $Fe_3(CO)_{12}$.

Investigators immediately seized upon these compounds for use in the explanations of phenomena of many varieties. Coke oven gas, furnace gas, illuminating and heating gases, among others, were found to contain iron carbonyls. The deposition of iron from the decomposition of the carbonyls on the hot fibers of the Welsbach gas mantles was offered as an explanation of lowered efficiency. Iron carbonyl was

found to exert an unfavorable action in the catalytic synthesis of methanol from carbon monoxide and hydrogen, and this introduced into the industry a problem in construction materials.

Iron carbonyls, nevertheless, remained of little commercial importance on their own account until 1924, when the use of iron pentacarbonyl as an "antiknock" for motor fuels created new interest in the compounds. Although lead tetraethyl was said to possess better antiknock properties, iron carbonyls were much less poisonous. Quantities were placed on the market in such forms as "Motalin." This connection with a most important industry stimulated and extended careful study of the properties of the iron carbonyls by many investigators.

Meantime, A. Joannis (*10*), in 1893, had prepared two interesting compounds, "potassium carbonyl," $K_2(CO)_2$, and "sodium carbonyl," $Na_2(CO)_2$. Guntz and Mentrel (*11*), in 1903, had prepared "barium carbonyl," $Ba(CO)_2$, and Roederer (*12*), in 1905, had prepared "strontium carbonyl," $Sr(CO)_2$. These unstable compounds were prepared by passing carbon monoxide through the solution of the appropriate metal in liquid ammonia. Von Bartal (*13*), in 1907, reported the preparation of an "aluminum carbonyl," $Al_2(CO)_2$. No further studies of these compounds appear to have been made. The reported behavior of the compounds leads to the general belief that they, like potassium carbonyl, are not closely related to the remaining carbonyls; in fact, they are not mentioned in most reviews of the subject.

By the use of high pressures and high temperatures, Mond, Hirtz, and Cowap (*14*), in 1908, prepared cobalt tetracarbonyl, which was later found to have the formula, $Co_2(CO)_8$; molybdenum hexacarbonyl, $Mo(CO)_6$; and the ruthenium carbonyls, $Ru(CO)$* and $Ru(CO)_2$.* By heating $Co_2(CO)_8$, they obtained $Co_4(CO)_{12}$. In accord with its empirical formula this compound received the name, "cobalt tricarbonyl."

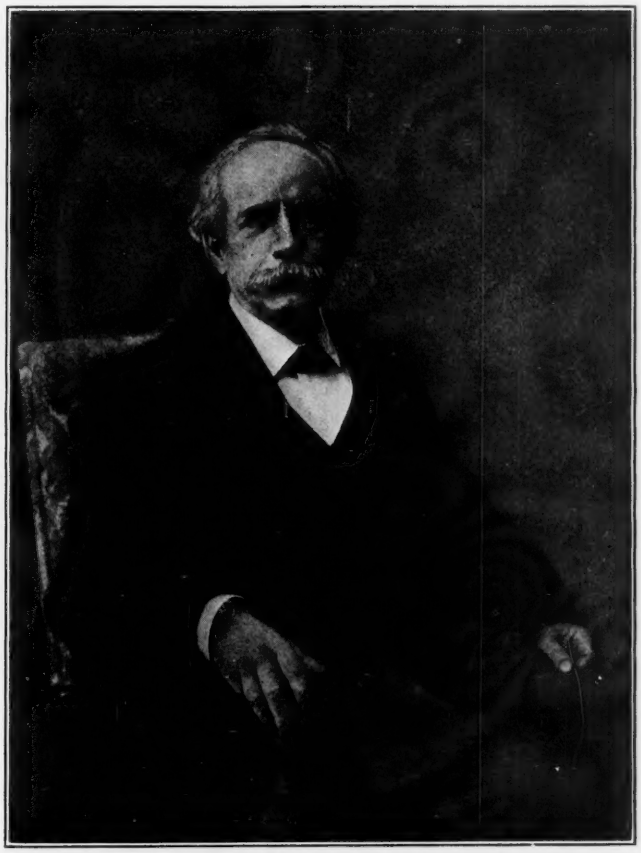
By the action of carbon monoxide on solutions containing metal salts and Grignard reagents, Job and coworkers (*15*) prepared chromium carbonyl, $Cr(CO)_6$, and tungsten carbonyl, $W(CO)_6$, as well as the molybdenum carbonyl earlier discovered by Mond.

In addition to these true metal carbonyls, many metal compounds have been prepared which contain the carbonyl radical, such as, $Cu_2Cl_2(CO)$, $Pt(CO)Cl_2$, $PtCl_2 \cdot 2(CO)$, $Pt_2Cl_4 \cdot (CO)_3$, $Fe(CO)_2(NO)_2$, $Co(CO)_3NO$, $K_4Fe(CN)_5CO$, $Fe(CO)_4 \cdot HgCl_2$, $Fe(CO)_2Cl_2$(phth†).

* Recently, Manchot and Manchot have prepared $Ru(CO)_5$, $Ru_2(CO)_9$, and another carbonyl, $Ru(CO)_x$, which appears to correspond to $Fe_3(CO)_{12}$ (*Z. anorg. Chem.*, **226**, 385 (1936)).

† Phth = orthophenanthroline.

Because of the limitations of space, we shall confine our attention principally to the true metal carbonyls and some of their derivatives.



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PIERRE-EUGENE-MARCELLIN BERTHELOT
1827–1907

The versatile French chemist, Berthelot, contributed to several fields of chemistry, and is also known as a historian of chemistry. He independently recognized the first carbonyl of iron and revealed several problems in the field of the metal carbonyls which still await solution.

Not less interesting in some cases than the discovery of carbonyls are the speculations concerning the possibility of undiscovered metal carbonyls. The familiar observation that copper appears to be carried along the hot tube when hydrogen or carbon monoxide is present in the gas stream has long suggested the possibility of a carbonyl of copper. Several attempts to isolate this compound, however, have met with failure. One of the most spectacular evidences of the presence of a copper carbonyl was perhaps that reported by Zelinsky (*16*), who found that bees, covered with copper oxide in a platinum boat, after being heated to about 450°C. in a combustion tube, were coated with copper in such a manner that minute details of structure were preserved. Zelinsky suggested that his method might be used for the metallization of larger animals, even of human be-

ings! Bertrand (*17*) proposed an explanation of these results in terms of a hypothetical copper carbonyl. This possibility was investigated by Mond and Heberlein (*18*), who were unable to obtain definite indication of the formation of copper carbonyl.

Courtesy of Mr. H. J. Pooley, General Secretary, Society of Chemical Industry

SIR JAMES DEWAR
1842–1923

Dewar was unusually well prepared for his comprehensive studies of the properties of the metal carbonyls. First interested in organic chemistry, next in spectroscopy, he turned in 1884 to low temperature studies, of which he left a memorial in his invention, the "Dewar Flask." "Characteristic of all his work was the elegance and simplicity of his methods."

The problem was also investigated by Frazer and Trout* without any certain indication of the presence of a carbonyl of copper. In these experiments carbon monoxide was passed over cuprous chloride and over cuprous acetylide at temperatures up to the point at which the latter compound exploded. Carbon monoxide was also passed through a suspension of cuprous chloride in formamide. It might be mentioned that attempts by these investigators to prepare cadmium carbonyl by several methods were also unsuccessful.

The possibility of the existence of carbonyls of platinum and palladium was first indicated in 1898 by the work of Harbeck and Lunge (*19*), who observed that platinum and palladium absorb respectively sixty and thirty-six times their volumes of carbon monoxide. Hydrogen did not displace the carbon monoxide from the metals, and in the case of platinum, the absorption product was stable, decomposing suddenly at 250°, liberating carbon monoxide. These facts strongly suggest the presence of a carbonyl of platinum and possibly of palladium. The compounds, if formed, were not volatile, and could not be extracted with the solvents tried. Mond, Hirtz, and Cowap (*14*) in 1910 were not successful in their attempts to prepare carbonyls of these metals by passing carbon monoxide under high pressure over the metals at high temperatures.

R. Mond (*1*) pointed out that the metals which form true carbonyls have low atomic volumes. This fact was used by him to predict the existence of a manganese carbonyl. His attempts to obtain such a compound, however, were not successful.

Pauling (*20*), from consideration of the quantum theory, predicted the possibility of the existence of $Pd(CO)_4$, $Pt(CO)_4$, $Ru(CO)_5$, $Os(CO)_5$, $Mn(CO)_5$, $V(CO)_6$, as well as $Co(CO)CN$, and $Mn(CO)_5CN$. At this time, any attempts to prepare these compounds, as far as the author knows, have remained either unsuccessful or unreported.†

II. PREPARATION

The metal carbonyls may be prepared by a number of general methods (*21*). Perhaps the most widely used method involves the passage of carbon monoxide over the finely divided metal at suitable temperatures and pressures:

$$x\,\mathrm{Me} + y\,\mathrm{CO} \leftrightarrows \mathrm{Me}_x(\mathrm{CO})_y$$

Successful application of this method has been reported in the preparation of $Ni(CO)_4$, $Fe(CO)_5$, $Co_2(CO)_8$, $Mo(CO)_6$, $Ru(CO)$, and $Ru(CO)_2$.‡ The temperatures and pressures required increase, and the yields decrease, in the order in which the compounds are given. The yields of all the carbonyls except those of nickel and of iron are small.

Much of the success of the process depends upon the previous treatment and the condition of the metal. Finely divided nickel may be prepared by reduction in hydrogen of nickel oxide at 400°, of nickel oxalate at 290–300°, or of nickel nitrate. The lower the temperature, in general, at which the nickel is reduced, the more active is the form of nickel obtained. In order to make the nickel more active it may be reduced upon pumice as a support. The presence of copper or iron in the nickel is said to increase the rate of formation of the

* Unpublished work.

† Since this was written, it is especially interesting to learn of the preparation by Manchot and Manchot of $Ru(CO)_6$.

‡ Manchot and Manchot recently prepared ruthenium pentacarbonyl, $Ru(CO)_5$, by this method. (*Z. anorg. Chem.*, **226**, 385 (1936).)

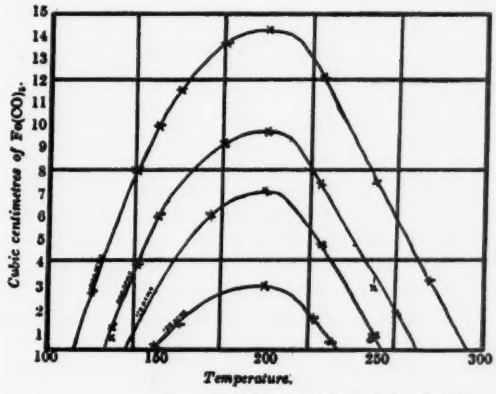
carbonyl. Very active nickel may be prepared by forming a nickel amalgam by electrolysis of a solution of nickel sulfate using mercury as a cathode, and subsequently distilling the mercury from the nickel at a low temperature in a vacuum (*22*). Carbon monoxide may then be passed directly into the vessel forming nickel carbonyl and sweeping the compound out of the reaction vessel, so that it may be condensed in a cooled bath (b. p. of $Ni(CO)_4$, 43.2°). If the nickel is very finely divided, the heat of reaction is sufficient to maintain the required temperature, which is about 30° to 100°.

Iron pentacarbonyl may be prepared by methods similar to those used in obtaining nickel carbonyl. The formation of iron pentacarbonyl by the action of carbon monoxide on the reduced iron is generally effected at about 173°, although temperatures as high as 400° have been reported. Above 200° the yield is reduced, apparently because of the carbonization of the carbon monoxide according to the equation, $2CO \rightarrow CO_2 + C$. The pressures used vary from 20 to 200 atmospheres, although here again the use of pressures as high as 1200 atmospheres has been reported. The relationship of yield to pressure and temperature has been studied by Mond and Wallis (*23*) and their results are indicated in Figure 2. Increase in temperature accelerates the reaction, and increased pressure prevents excessive decomposition of the carbonyl. Above *ca.* 200° the metal catalyzes the disproportionation of carbon monoxide to form carbon dioxide and to deposit carbon on the iron; this side-reaction lowers the rate of formation of the carbonyl.

The presence of oxygen hinders the reaction, as does also an oxide coating on the iron. Addition of finely divided alumina, bismuth, nickel, or copper, prevents sintering of the metal and accelerates the reaction. Ammonia, hydrogen, and small quantities of sulfur compounds in the carbon monoxide exert a favorable influence on the rate of formation of the carbonyl.

In one industrial process for the manufacture of iron pentacarbonyl, carbon monoxide is passed at pressures varying from 50 to 200 atmospheres over iron (obtained, for example, by reduction of the oxide) held at temperatures between 100° and 200°. The same results may be obtained by the use of water-gas, which contains hydrogen and carbon monoxide. The exothermal reaction between the carbon monoxide and the iron supplies the heat necessary to maintain the temperature required for the production of the carbonyl. The flow of gases may reach five hundred liters an hour. The iron pentacarbonyl, constituting about ten per cent. of the gases issuing from the reaction chamber, is condensed, and the excess carbon monoxide is returned to the reaction vessel. The liquid carbonyl is usually purified by distillation in a low boiling hydrocarbon such as benzene or kerosene, forming a solution in which the carbonyl is marketed.

In the commercial preparation of iron pentacarbonyl a number of ingenious modifications of this method have been patented. For example, iron turnings or even scrap iron may be oxidized by air, or steam, or both, and then reduced, either with hydrogen, or directly with carbon monoxide. Iron oxide or chloride may be reduced with hydrogen at 200° to 400° and under pressures of 20 to 1200 atmospheres. Pyrites, FeS_2, may be converted in the presence of wood charcoal at 1000° into Fe_2O_3, which is subsequently reduced by carbon monoxide. Iron carbonyl is formed at 173° and 180 atmospheres. The use of ashes to support the metal is



Courtesy of Journal of the Chemical Society

FIGURE 2.—A CHART SHOWING THE INFLUENCE OF TEMPERATURE AND PRESSURE ON THE YIELD OF IRON PENTACARBONYL

said to increase the yield. Iron ores also may be reduced by means of other solid or liquid carbonaceous materials. In these processes the carbon monoxide which is formed produces the carbonyl in one operation. A modification of the above procedure is found in the reduction of ferric hydroxide sludge or Norwegian iron ore with lignite.

Processes have been patented in which carbon monoxide is passed over fine red pyrites which is either mixed with paraffin to form a paste, or suspended in benzene or liquid iron pentacarbonyl, through which carbon monoxide is passed. In like manner nickel carbonyl may be obtained by passing carbon monoxide through suspensions of the metal (and according to patents, also the carbonate, or the oxide) in inert liquids, such as paraffin oils, and methyl naphthalene.

Of special interest is the favorable influence of compounds of sulfur on the formation of nickel, iron, and cobalt carbonyls. It is well known that sulfur compounds are poisons for certain catalysts, and it might be thought that the presence of sulfur compounds would lower the activity of the finely divided metal from which the carbonyl is made. This, however, is not found to be true. Manchot and Gall (*24*) found that nickel carbonyl formed readily when carbon monoxide was passed through an aqueous solution of nickel sulfide. They gave indication that the cyanide would serve equally

well. As promoters of the reaction of the finely divided metals with carbon monoxide, COS, CS_2, C_4H_4S, active forms of sulfur, selenium, and tellurium, and even sulfur dioxide have been reported in various patents (*25*). Blanchard and his co-workers (*26*) studied the preparation of carbonyls in solutions of sulfides, selenides, and cyanides of nickel and cobalt, and suggested as an explanation that a potential dissociation of nickel and sulfur, for example, was augmented by the presence of sulfur removing agents, causing the nickel potential to rise to the point of carbonyl formation, according to the equilibrium relationships,

$$NiS \leftrightarrows Ni + S\ ;\ K = \frac{C_{Ni} \times C_S}{C_{NiS}}$$

$$Ni + 4CO \leftrightarrows Ni(CO)_4;\ K = \frac{C_{Ni(CO)_4}}{C_{Ni} \times (C_{CO})^4}$$

Recently, Blanchard and Coleman (*27*) have reported that the absorption of carbon monoxide by alkaline cobalt salt solutions is promoted by the presence of cystine, tartrate, and several amino acids, as well as by the presence of cyanide and sulfide ions.

Frazer and Trout* passed carbon monoxide through alkaline suspensions of nickel chloride, nickel sulfate, nickel oxalate, and cobalt chloride in purified formamide and were able to obtain evidence of formation of carbonyls of nickel and cobalt. However, carbonyls did not form in the absence of potassium hydroxide. The investigators interpreted these results as due to the formation of an alkaline cyanide suspension resulting from the slight decomposition of the formamide into water and hydrogen cyanide.

An unusual preparation of nickel carbonyl may also be mentioned (*28*). To nickel chloride or bromide in ligroin, sodium in shot form is added. The mixture is then heated on a water bath to 90° and oxalic acid ethyl ester is added. The carbon monoxide liberated forms nickel carbonyl which may be condensed in a cooled outlet tube.

* Unpublished work.

A quite different method of preparing metal carbonyls was discovered by Job and his co-workers (*15*). They passed carbon monoxide into ether solutions of Grignard reagents to which had been added salts of nickel, chromium, tungsten, and molybdenum, and obtained evidence of the formation of the carbonyls of these metals. They isolated $Cr(CO)_6$, $W(CO)_6$, and $Mo(CO)_6$ in small yields. This method of preparation has been studied by Hieber (*29*), who has made a tentative suggestion that the mechanism must involve a disproportionation of intermediate carbonyl compounds low in carbon monoxide during the hydrolysis of the solutions. Among other equations he offered the following as an illustration.

$$3Cr(CO)_3A_3 + 6H^+ \longrightarrow Cr(CO)_6 + 2Cr^{+++} + 9A + 3CO + 3H_2^+ \ldots$$

"A" represents a neutral molecule which is liberated along with carbon monoxide and hydrogen when the solution is hydrolyzed. The carbon monoxide liberated is believed to be activated and to form the pinacones, ketones, etc., found among the by-products.

In conclusion, additional isolated preparations should be mentioned which make use of certain reactions of the metal carbonyls themselves. For example, iron enneacarbonyl, $Fe_2(CO)_9$ (*7*), is prepared by the action of light on $Fe(CO)_5$, with the liberation of carbon monoxide. By heating $Fe_2(CO)_9$ (*8*, *28*) in solution in ether, benzene, etc., a green solution of $Fe_3(CO)_{12}$ is formed without liberation of carbon monoxide. On exposure of this solution to light, $Fe_2(CO)_9$ is again obtained. $Fe_3(CO)_{12}$ arises also as one of the products of the action of alkali on $Fe(CO)_5$ and is obtained in the decomposition by acids of some substitution products of the iron carbonyls, especially the tricarbonyl compounds, which will be discussed briefly at a later time. As mentioned before, the jet black crystals of $Co_4(CO)_{12}$ are obtained by heating $Co_2(CO)_8$ to about 60° (*13*).†

† Manchot and Manchot prepared $Ru_2(CO)_9$ from $Ru(CO)_5$ by the exposure of this compound to light, or by heating it to 50°. $Ru(CO)_x$, which may be the analog of $Fe_3(CO)_{12}$, is formed as a by-product when $Ru(CO)_5$ is converted into $Ru_2(CO)_9$. (*Z. anorg. Chem.*, **226**, 385 (1936).)

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J. J. VAN LAAR*

AS HOLLEMAN is the dean of Dutch organic chemists, so van Laar may be rightly called the Nestor of Holland's physical chemists. Pupil, friend, and co-worker of distinguished Dutchmen (van't Hoff, van der Waals, Bakhuis Roozeboom, Lorentz, Kamerling Onnes), van Laar is one of the few (if not the last) remaining links between the past and the present generation of Dutch physical chemists. There are very few people who can expect to be active beyond three score and ten and publish, as van Laar did at seventy-five, an opus magnum embodying the results of many years of unremitting labor in one's chosen field. In this age of ours where chemical thermodynamics is taught at all the leading universities and colleges and "Lewis and Randall" has become a household word to every student majoring in physical chemistry, we are apt to overlook the pioneers of whom van Laar was one of the most prominent. It is nearly forty-five years ago since he published (in Dutch) a treatise on "Thermodynamics in Chemistry." His "Six Lectures on the Thermodynamic Potential," written in 1906 (in German, translated into Italian and into Russian but never into English), are as readable today as they were thirty years ago. Ideas which are now universally accepted, such as the complete dissociation of strong electrolytes, were proposed by van Laar in 1900, but, as he himself philosophically reminds us, the trail blazers are often forgotten. An ardent admirer and advocate of Gibbs, van Laar seems to have found the least recognition in the homeland of the celebrated author of the phase rule. The reason may be, at least in part, the language barrier, most of van Laar's publications having been written in Dutch, German, or French. Furthermore, his connection with the University of Amsterdam was of comparatively brief duration. Ill health forced him to go to Switzerland in 1912. Here he has been busy ever since, as witness the list of over one hundred articles published in various journals. Born in 1860, he was sent, at the age of sixteen, to the Dutch Naval Academy, but, like Michelson, he quit the navy after a few years to embark upon a scientific career. In 1881 he enrolled as a student in the University of Amsterdam where he remained till 1884. After a dozen years of high-school teaching, first at Middelburg, and later at Utrecht, he went back to Amsterdam where he was admitted to the University as "privaat dozent." In 1903 he became officially connected with his alma mater, first as an assistant to Roozeboom and later as a lecturer in theoretical chemistry. Although he has been a resident of Switzerland for the past twenty-five years, van Laar has found due recognition in his native country. In 1914 the University of Groningen conferred upon him the honorary degree of doctor of science. In 1929 he received the Bakhuis Roozeboom medal; in 1930 he was made corresponding member of the Royal Academy of Sciences; and in the following year the Dutch Government made him a chevalier of the Order of the Dutch Lion. Mentally alert and active, and still in the midst of scientific productions, van Laar looks upon his present status in life as "la fleur de l'age," which, as his friends confidently expect, will last well beyond four score.

(*Contributed by H. S. van Klooster, Rensselaer Polytechnic Institute, Troy, New York*)

* See frontispiece.

On STARCH

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THE availability and low price of starch and starch derivatives have led to the notion that the chief use of these substances is that of diluent or cheapening agent for worth-while products. The notion is erroneous!

In the following paragraphs some of the many and varied uses of starch are noted and the characteristics of starch and starch derivatives are described.

DEFINITIONS RELATING TO STARCH AND STARCH PRODUCTS

1. *Starch*, the native carbohydrate, is made in the following ways:

(*a*) Corn starch. The kernel is crushed; the germ is separated; the starch is "tabled"—that is to say, allowed to settle out in long channels down which a water suspension of the starch slowly flows. The water contains a small quantity of free sulfur dioxide left over from the crushing operation where the sulfur dioxide is used to soften the kernel.

(*b*) Potato starch. The tuber is pulped; the starch is separated in settling tanks after the coarse material has been removed by a series of screenings. The same method is used, at present, for the manufacture of sweet potato starch which is still in the experimental stage.

(*c*) Tapioca (manioc) flour. The dried roots of the manioc plant are skinned and ground. The coarse material is screened out. From the fine screenings the starch is isolated by tabling.

(*d*) Sago starch. The pith of certain varieties of palm is beaten to a fine slurry in water; the slurry is screened and air-dried. After grinding, the pith is suspended in water and settled or "tabled" to obtain the starch.

(*e*) Wheat starch. Wheat flour is the starting material. The separation of the gluten from the starch is accomplished in one of two ways. The older method is to ferment the gluten in a two-week fermentation and to recover the starch from the fermented mass by "tabling." The more modern way is to form a dough ball from the flour. The dough ball is kneaded on a screen by rollers while water is sprayed upon the mass. The gluten forms the characteristic mass which sticks on the rollers and the screen while the starch is washed out by the streams of water, through the screen and into a settling tank. The gluten is recovered for incorporation in high protein cattle feed.

(*f*) Rice starch. The heads of starch are subjected to rough screening to remove the hulls. The kernels are softened by alkaline steeping before they are ground. The soft mush resulting from the grind is then put through screens, after which the starch is separated therefrom by tabling out.

2. *Dextrins*, for present purposes, are considered to be the conversion products of starch effected by the application of heat thereto either in the presence or absence of acids. They include British Gums, conversions made by simple roasting; those made in the presence of a large quantity of water; those made by spraying moist starch on hot rolls and causing the starch to gelatinize by heat and pressure; and conversions made by steam. It is generally believed that dextrin is a degradation product of starch, effected by changing the complex starch molecule into something simpler, even though both the structure of the starting material (starch) and the end-product (dextrin) are still unknown. It follows that many series of dextrins can be obtained by gradually varying the rigor of the degradation process.

3. *Oxidized and Chlorinated Starches* are derivatives of starch produced by the treatment of native starch with an appropriate reagent from the group: alkaline or alkaline-earth metal peroxides, hydrogen peroxide, and alkaline hypochlorites. The hypochlorites are practically the only agents in commercial use at the present time. As in the case of the dextrins, a variety of products may be obtained by varying the concentration of the reagent, and the time and the temperature of the reaction.

4. *Thin-boiling starches.* In the textile industry a starch of good body but low viscosity is desired. Starches are treated with acids of varying strengths at low temperatures. The duration of the treatment is conditioned by the characteristics of the desired product.

PROPERTIES

The several varieties of starch and dextrin and their several derivatives have many comparable characteristics which distinguish them and make them suitable for industrial purposes. The following properties are particularly noteworthy.

1. *Moisture content* is defined as the loss of weight of a sample which is dried for a specified time at a definite temperature, for example, for four hours at 105°. In native starches, as found in commerce, this value is from eight to twelve per cent. In dextrins the value is considerably lower; and, although dextrins have a tendency to pick up moisture slowly, they seldom attain values which are characteristic of the native starches.

2. *Solubility.*—Starches are very insoluble in water; dextrins can be prepared with any desired solubility varying from very low values to very great solubility in

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water. Solubility is measured as the percentage of a sample which will dissolve in a specified quantity of water. Unfortunately, the temperature and the ratio of solute to solvent are not yet matters of standard practice in different laboratories.

3. *Gelatinization* is the disintegration of the starch particle in the presence of water or some other solvent. Gelatinization may be accomplished by (*a*) prolonged agitation, (*b*) heating, (*c*) the addition of alkali. The stages of gelatinization are continuous from the initial swelling until the final rupture of the starch cell. For a detailed microphotographic study of gelatinization the reader is referred to the work of Sjostrom (*1*). The problem of gelatinization is discussed more fully later on when the possible structures for starch are considered.

4. *Viscosity* denotes the fluidity of the starch gel and is measured at a definite temperature (which unfortunately is not the same with all investigators) after the starch or dextrin is gelatinized. Many methods for measuring viscosity are in use; the usual method is to measure volume of efflux of a sample through a standard orifice, with a constant pressure head, in unit time, at standard temperature.

5. *Fluidity* is another definition of viscosity but is generally applied to the determination made on cold gelatinized solutions of starch or dextrin made by the addition of alkali. This cold gelatinization will be mentioned later in connection with a discussion of the theory of gelatinization.

6. The *Setting-up* characteristic of starch is a property which is best described as a large increase in viscosity of the starch "solution" on standing. The setting-up is therefore substantially the conversion of the fluid gel to a more or less rigid structure. This property is observed in all varieties of starch, but it occurs only to a limited degree in high-grade tapioca flour and certain oxidized starches.

7. *Acidity* is measured in terms of the number of milliliters of $N/10$ alkali required to neutralize a five-gram sample of the starch suspended in a convenient quantity of water and titrated to a phenolphthalein end-point. The final result is expressed as the percentage of free hydrochloric acid in the sample. Native starches have a very low acidity, depending upon the care with which they were washed during their preparation. Dextrins, depending upon their mode of preparation, usually run higher than starches.

8. *Tackiness* is that property of a starch or dextrin solution which causes it to be sticky while wet.

9. *Adhesion* is that property of starch or dextrin solutions which causes them to form a firm bond between two solid surfaces after drying.

THE UTILIZATION OF STARCH AND STARCH PRODUCTS

The wide industrial utilization of starch and its derivatives is fundamentally determined by one or more of the following:

(*a*) the availability of starch as a carbohydrate for nutrition and fermentation;

(*b*) the adhesive strength of starch films; and

(*c*) the body and stiffness imparted to fibers by a starch gel.

Foods.—Starch is used as an ingredient of pudding powders, salad dressings, meringue powders, soups, candy, and many other foodstuff preparations. It is used in baking, in the manufacture of dextrose, and for part of the fermentable carbohydrate in brewing. For most of these purposes almost any of the available starches can be employed. In the United States, the low cost of corn starch makes its use almost universal except where a specially clear stable product is desired. For superior products and for stabilizing chocolate milk, a high-grade tapioca flour is used, although for the latter purpose locust-bean and sodium alginate preparations are now preferred.

Adhesives.—It is because of their adhesive qualities that starches and dextrins are ubiquitous in their distribution through industry. The adhesives are usually alkaline; for special products, such as envelopes, neutral or acid adhesives may be made.

Library paste is generally made from potato starch; it is preserved by inclusion of phenols or formaldehyde, and kept from drying by inclusion of a hygroscopic material, for example, glycerol, invert sugar, or commercial glucose. *Envelope seals* are made from tapioca dextrins which regain their tackiness upon being wetted. These dextrins are also used in the adhesive film on *postage stamps*. *Foundry mixtures* are special dextrins which hold the sand molds together during the casting operations. A good *tin paste* solves the problem of sticking labels on cans and, generally, paper to metal. Tin pastes are special corn and tapioca dextrins and usually contain also an acid ingredient. *Laminated paperboard* depends upon heavy dextrins, as well as animal glue, for successfully keeping its layers stuck together.

Corrugated board depends upon starch adhesives to an ever-increasing extent for binding the liners to the fluted straw. Corrugated board can be made continuously by using an aqueous gelatinized starch medium which carries some ungelatinized starch. The places at which the seals are made are heated to gelatinize at these places the ungelatinized starch, with the formation of an extremely strong bond. This is a recent development of J. V. Bauer (*2*). The resulting board is neutral in reaction, and the new process has many operating advantages over the older practice which utilized alkaline sodium silicate.

Carton sealing, label pasting, boxmaking, gummed labels, bagmaking, and gummed tape are other examples of the applications of dextrin adhesives. In each case the adhesive must be "tailored" to the surfaces which are to be sealed.

Borax is added to starch and dextrin adhesives to increase their tackiness and to make the body of the finished water solution heavier. Concentrations of from ten to twenty-five per cent. of borax or borosoap (based on the dry starch or dextrin) are blended with the adhesive. The action of borax and borosoap are

more or less specific among the alkaline buffers. There is an additional thickening effect when soda ash and caustic soda are used; they cause a marked increase of viscosity, such as is noted for borax, but when such alkali-containing adhesives are used there is also a tendency for the finished adhesive to roll off the surface to which it is being applied instead of forming a smooth film. Hence, although blends of borax and the stronger alkalies are used, the concentration of the stronger alkali is kept low, and seldom if ever exceeds two per cent.

The already noted fact, that starch is gelatinized by sodium hydroxide at ordinary temperatures, finds important application in the manufacture of cold water and ready mixed starches for industrial use. Here, also, the caustic soda is kept to a minimum.

Urea possesses the valuable property, when incorporated in a starch or dextrin, of reducing the amount of water necessary to completely gelatinize a starch with the production of a freely flowing solution. Thiourea and other carbamide derivatives possess this same property; the economics of the manufacture of adhesives, however, dictates the use of the cheapest material, urea. No explanation of the behavior of the carbamide derivatives is attempted at the present time.

Starch Gels.—It is in papermaking and textile sizing, the largest consumers of starch products, that the gel-forming property of starch, chlorinated starch, and the dextrins is most important. In these very large fields the product must be adapted to the standard method of production.

In *papermaking* there are several steps which utilize starch products; for convenience they can be classified as (*a*) sizing the fiber before the sheet is formed, (*b*) sizing the paper after the sheet is formed but while it is wet, and (*c*) coating the paper. Papermaking requires the unimpeded flow of liquids until the sheet is formed either on the Fourdrinier wire or on the cylinder. Hence anything put into the fiber-water mixture must not materially affect the consistency of the said mixture. After the sheet is formed it can be treated by flowing a starch solution out upon the sheet. As the sheet is carried along by the wire, it can be treated by immersion (tubbing), and it can be coated.

In sizing paper fibers before the sheet is formed a wide choice of starches is available. "For use in the beating engines various kinds of starch are available but the one used is generally that which can be obtained most cheaply, due regard being paid to quality. For this reason corn starch is used almost entirely in this country..." "The starch is added to the engine either in the raw condition or after boiling with water to form a paste" (*3*). The retention of the starch is problematical, but retention in excess of fifty per cent. for raw starch and forty per cent. for cooked starch is claimed when ten per cent. starch is added to the stock (*3*), but the figures are probably high. Although the starch-sized paper is not waterproofed, as when a rosin size is used, all the other desirable features of a size are present, *viz.*, hardening, elimination of fuzz, and increase in strength. However, starch may be used in conjunction with a rosin size.

Ordinary starch gels are too viscous for surface sizing but chlorinated starches are quite satisfactory and are used. It is characteristic of the chlorinated starches that they yield sols of much greater fluidity than other types of starch. After calendering, the paper shows the characteristic firmness and rattle (a very valuable property) of tub-sized paper. To obtain surface hardness, rattle, dust-proofing, general strengthening, and hardening, both beater starch and a surface sizing may be and are employed.

In coating paper two requirements arise and starch can meet them. Clay must be bound to paper so that it does not dust off, and, secondly, a flexible film must be formed so that the coating does not crack. These needs are met by an oxidized starch which carries clay in a thin slurry (to eliminate brush marks from the spreading brushes) and yet gives a firm bond when dried out. The chief advantage accruing to starch-coated papers is not to be found in the making of the paper although the advantages there are considerable; it lies in the use because starch-coated papers require no slip sheeting in printing. The present outlook is for starch derivatives to largely replace the casein coatings now in use.

The textile industry is the largest consumer of starch. For reasons similar to those set forth for sizing paper fibers, textile fibers are millsized. Originally, plain starches were employed; the trend now is overwhelmingly in the direction of thin boiling starches and the chlorinated starches.

The sizing is done either at the thread stage or after the cloth is made. Various dispersing agents, softening agents, and penetrants are used in conjunction with the starch. The principle is apparent without further elucidation. The mechanism is one of film formation around each fiber without making the entire fabric impervious to air or moisture.

THE GELATINIZATION OF STARCH AND ITS DERIVATIVES

Study of starch under high magnification (900) reveals a skin, a distinct outer layer, and an inner portion. Chemical separation by dexterous manipulation of the gelled starch (for example, potato starch) results in two fractions. One of these contains phosphoric acid while the other is phosphoric-acid free. According to Samec (*4*), when potato starch is gelatinized ninety-five per cent. of the amylo-phosphoric acid is found in the gel phase. As starch gelatinizes, radial cracks develop during the swelling, eventually the skin bursts and the particle is disintegrated. This interior swelling may be attributed to a hydrating catalyst such as an inorganic acid which is attached to the carbohydrate. The low phosphoric-acid content of corn starch would seem to demand that the activity be catalytic to explain the hydration by interior swelling; the presence of the amylo-phosphoric acid in the gel phase seems to bear out this contention.

Amylo-phosphoric acid is not the only hydrating influence; this may be shown by the action of caustic soda on starch whereby the starch is gelatinized, although it is an open question whether the alkali exerts its effect

through the amylo-phosphoric acid, or directly on the acid-free carbohydrate. That an intermediate mechanism is involved is indicated by inhibition phenomena. Treating starch with ethanol inhibits the gelatinization and *ipso facto* can be considered to be acting on the hydrating mechanism; action on the substrate is yet to be discovered.

Sjostrom (*1*) presents very clearly the evidence that starch particles are not only built up of concentric skins like an onion (based upon the manner of aqueous disintegration of dextrins) but also along radial lines (based upon the microphotographs of the gelatinization process). Sjostrom (*1*) suggests (after A. Meyer (*5*)) that perhaps the manner of pre-treatment of the starch determines the manner of cleavage and the properties of the resulting gel. This is a very interesting speculation which is open to experimental verification; it is to be hoped that such experiments are in progress.

SUMMARY

1. The sources and derivatives of starch have been enumerated.

2. The industrial applications of starch and its derivatives have been pointed out.

3. The gelatinization of starch has been discussed.

ACKNOWLEDGMENT

I am indebted to Mr. H. F. Bauer for his criticism and suggestions and to my favorite and severest critic who prefers to remain anonymous.

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A STATISTICAL ANALYSIS *of* SOME QUANTITATIVE EXPERIMENTS *in* ELEMENTARY CHEMISTRY

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IN MANY courses in elementary chemistry it is customary to introduce experiments of a quantitative nature. There is a wide choice of suitable experiments of this sort. Some of the commoner ones include determinations of molecular weights, equivalent weights, formulas of compounds, percentage of water of hydration, solubility, etc. These experiments are usually carried out by students with little laboratory experience, and the methods used must be necessarily rather simple and adaptable to fairly large groups. If the results obtained are not reasonably quantitative, the experiment fails to accomplish the purpose for which it was designed. Therefore, the degree of success obtained with average groups of students in handling experiments involving a quantitative result is of interest.

A number of years ago the writer attempted to throw some light on this problem by tabulating the data obtained in certain quantitative experiments in the laboratory classes in beginning chemistry at Brown University. Analysis of these gave the information which is presented here. A similar group of data has been published by Farquhar and Ray.[1]

The experiments studied were as follows (1) the molecular weight of carbon dioxide, (2) percentage of oxygen in the air by volume, (3) the equivalent weight of zinc, (4) the formula of a sulfide of copper.

THE MOLECULAR WEIGHT OF CARBON DIOXIDE

In this experiment, a 250-ml. flask with a rubber stopper fitted with a capillary tube was weighted to the nearest milligram on an analytical balance of a sort

[1] FARQUHAR AND RAY, "Proficiency of first-year students in quantitative experiments," J. CHEM. EDUC., **13**, 74–5 (1936.)

that might be used safely by a beginning student. The flask was then filled with CO_2 from a tank of the compressed gas. By looking across the top of the flask toward the light the overflow of gas could be observed when it was filled. The stopper was then inserted, the flask allowed to stand for about ten minutes and weighed again. The flask was next filled with water and weighed on a pan balance to the nearest gram. This gave the volume of the flask and knowing the temperature, pressure, and weight of the CO_2 the weight of 22.4 liters at standard conditions was calculated.

The results of one hundred thirty-five students over a period of three years are given in the frequency-distribution curve of Figure 1. This familiar type of curve, called a histogram, reports frequency in results plotted against the result for that frequency $\pm$ 0.25. Thus, the second block to the right of the broken line indicates that twelve students obtained the result 45 ± 0.25. The broken line gives the theoretical result for the molecular weight of carbon dioxide as 44.

Examination of the diagram shows that forty-three per cent. of the results are greater than the value 44.25, and fifty-seven per cent. are less. This indicates a slight tendency toward low results. Acceptable results may be said to lie from the 41.5 block to the 45.5 block, as at these points the curve begins to taper off. Within these limits about fifty-three per cent. of the results are below 44, and forty-seven per cent. are above. Considering the total number of results, sixty-six per cent. of these would lie within the acceptable limits, while twenty-two per cent. show the best ability by being within the 44 block.

From the distribution of results for this experiment it appears that the chance of getting an excellent result is about one to four. The experiment may be judged to be wholly satisfactory for the beginning student.

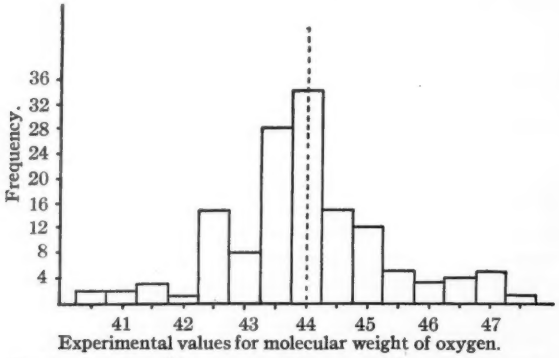

FIGURE 1.—THE MOLECULAR WEIGHT OF CARBON DIOXIDE

PERCENTAGE OF OXYGEN IN THE AIR BY VOLUME

An hydrometer jar was filled with water and in this was placed a glass tube about 25–30 cm. in length with a constriction about 2 cm. from one end. This held a small piece of phosphorus. A 100-ml. gas measuring tube was filled with water, inverted in the hydrometer jar, and 40–50 ml. of air were let in by tipping the bottom of the tube. The volume was noted, the tube lowered over the phosphorus, and allowed to remain there until the next laboratory period (one week). The new volume was then read. Both volumes were converted to the same temperature and pressure and from these volumes the percentage oxygen by volume was calculated.

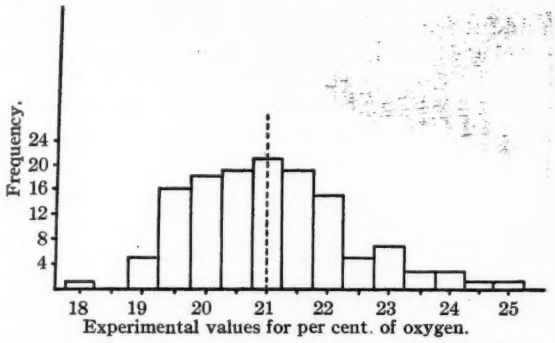

FIGURE 2.—PERCENTAGE OF OXYGEN IN THE AIR BY VOLUME

The frequency-distribution curve for one hundred thirty-seven results obtained in this experiment is given in Figure 2. Three results above 25.7 are not shown. The broken line represents the theoretical percentage of oxygen in the air by volume as approximately twenty-one per cent.

This curve shows a different type of distribution from that given in Figure 1. It is much flatter, with the general tendency toward neither high nor low results. Forty-nine per cent. of the results are less than 21 ± 0.25 and fifty-one per cent. are greater. Sharp breaks occur at 19.25 and 22.25. Eighty per cent. of the results lie between these values. This would indicate that acceptable results should have the value 21 ± 1.7. The curve shows the possibility of about one person in six of obtaining 210 ± 0.25.

THE EQUIVALENT WEIGHT OF ZINC

A small piece of zinc wire (about 0.100 g.) was weighed to the nearest milligram on an analytical balance. About 20 ml. of concentrated hydrochloric acid was put into a 50-ml. gas measuring tube and then filled completely with water without mixing. A short piece of thread was tied to the zinc which was then lowered into the tube and held in place by a one-holed rubber stopper or notched cork. The whole was inverted in a hydrometer jar filled with water. The volume of hydrogen released was measured by adjusting the water levels. After correction was made for aqueous tension, temperature, and pressure the equivalent weight of zinc was calculated.

The results obtained in this experiment (one hundred thirty-seven results with two not shown) are given by Figure 3. The broken line indicates the theoretical result to be 32.7. Of the results to the right and left of the block cut by this line about twenty-eight per cent. are less than 32.25 and seventy-two per cent. are greater than 32.75. This shows a tendency for high results which might be accounted for by the fact that the zinc was probably impure.

The distribution on either side of the highest block is, as should be expected, about fifty-one per cent. being less than 32.75, and forty-nine per cent. greater than 33.25. One may conclude that a result of 33 ± 0.25 is excellent; 33 ± 1.75 is satisfactory, and deviations greater than this as unsatisfactory. Within these limits there are about eight or nine chances in ten of getting acceptable results, and about one in five of getting excellent results.

Farquhar and Ray give a distribution curve for a similar experiment on the equivalent weight of aluminum. Their curve shows deviations of about one hundred parts per thousand as acceptable while the curve here indicates that for zinc deviations should be not more than fifty parts per thousand. Strangely enough, their curve shows a tendency for low results, rather than for high results. Also, the distribution is not as uniform as shown here. This is due, probably, to a different technic which appears to be not as satisfactory as the one described here.

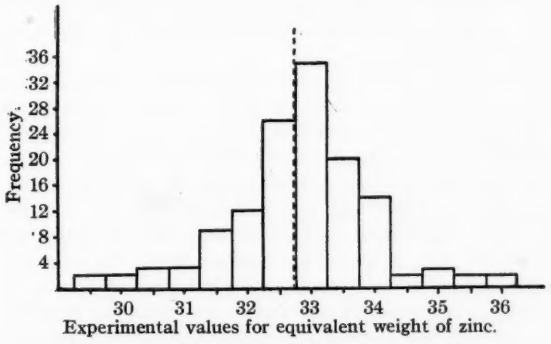

FIGURE 3.—THE EQUIVALENT WEIGHT OF ZINC

FORMULA FOR A SULFIDE OF COPPER

A small, hard, glass test-tube was cleaned, dried, and weighed on an analytical balance. About 50 cm. of No. 22 copper wire was folded into four parts and wrapped in a spiral that would just fit the test-tube. The test-tube and spiral were then weighed together. The copper was covered with sulfur and heated in a Bunsen flame until all excess sulfur had been driven out. This heating usually takes from fifteen to twenty minutes. The tube was then cooled and weighed. From the recorded weights the per cent. of copper and sulfur was calculated, and from these the formula determined.

Figure 4 gives the tabulation of one hundred twenty-nine results. Ten results, not shown, fall outside the limits defined by the graph. The broken line represents 79.9 as approximately the theoretical result for the percentage of copper in the compound (Cu_2S).

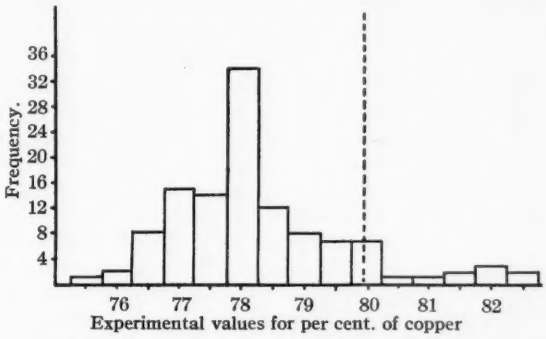

FIGURE 4.—FORMULA OF A SULFIDE OF COPPER

It can be seen that the results are decidedly low. Of the total to be right and left of the 80 ± 0.25 block about eighty-seven per cent. are less than 79.75, and thirteen per cent. are greater than 80.25. This low result is scarcely surprising, for, no doubt, some of the cuprous sulfide is converted into cupric sulfide.

Since the chances for obtaining a theoretical result are small (less than six per cent. of the total results lie within 80 ± 0.25 range) the analytical side of the experiment should not be emphasized. The primary object of the experiment was to obtain data which would give the formula Cu_2S. The results show that it is entirely satisfactory for this purpose.

It is interesting to compare the data here with the data for the same experiment as given by Farquhar and Ray. The type of distribution is almost identical except that the highest frequency occurs at 79, rather than at 78 ± 0.25 as shown here. The tendency toward low results is shown in both cases. They report fifty per cent. of the distribution falling between 76 and 81, while Figure 4 shows about eighty-two per cent. falling within similar limits. The significant limits of the distribution given here fall between 76 and about 80.5 while Farquhar and Ray extended theirs from 72 to about 83.

No doubt there are other experiments of a similar nature which are capable of giving more accurate analytical results. For example, the decomposition of silver nitrate, or the formation of zinc sulfide, may be mentioned. It would be of interest to analyze these or similar experiments in the manner outlined here.

The PREPARATION *of* TEACHERS *of* CHEMISTRY*

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THE vigorous controversy of recent years concerning the preparation of teachers arises in part from the fact that members of academic departments and professional educators often consider the problem from widely divergent and more or less biased points of view. As pointed out recently by E. R. Hedrick,[1] Professor of Mathematics, the University of California at Los Angeles, this situation is unfortunate and may lead to serious consequences to all concerned. The solution, in his judgment, lies in open-minded inquiry, in sincere study and discussion of the basic issues involved, and in hearty coöperation of both groups in reorganizing and improving programs for prospective teachers. Such conferences as the one in which we are now engaged provide excellent opportunities for the identification of basic issues and for the clarification of thinking. In harmony with the plan adopted when this conference was arranged, my discussion will emphasize various types of preparation which are dictated by the total service which teachers of chemistry render.

An analysis of recent literature on the preparation of teachers leads to the conviction that much of the discussion is beside the point. Similar criticisms may be made concerning the terms in which certification requirements are expressed. All too frequently the chief problem considered relates to the number of courses that should be taken in education and in subject-matter fields. Obviously discussions and certification rules which are concerned merely with quantitative requirements are of little value. The fundamental problems which we face today are qualitative in character and relate primarily to the nature of the preparation essential to insure well-educated teachers who are competent to render the various types of service which society delegates to them today.

Before attacking the basic problem suggested above, I wish to present five statements which will be assumed in the discussion that follows, namely:

1. that we are concerned primarily on this occasion with the preparation of teachers at the secondary and junior-college levels;

2. that we are concerned with all elements of their college and university curriculums that promote efficiency as teachers, as well as that portion of it which insures adequate breadth and depth of preparation in the field of chemistry;

3. that in harmony with current practice the teacher of chemistry must be prepared to teach at least one additional subject or field;

4. that he must be prepared to serve also as an efficient member of a faculty that is charged with the responsibility of determining intelligently the policies, organization, curriculum, and teaching procedures of an institution that is devoted primarily to the extension of general education; and

5. that curriculums for teachers of any subject must be revised at frequent intervals in harmony with changing social needs and the broadening purposes of public education. Evidence exists that needed reforms can be effected at times only through more or less radical departures from current practice. We face such a period today with respect both to the academic and the professional preparation of teachers. In support of this assertion, brief reference will be made next to recent social developments which directly affect teaching.

During the last two decades impressive social and economic changes have occurred. Industrial and commercial agencies have multiplied on every hand. Urban population has increased by leaps and bounds. The products of science and invention have radically modified habits and standards of living. New social attitudes, ideals, and relationships have developed. As a result of these and other significant changes we are living today under conditions which present distressing problems, as well as many advantages. The economic crisis through which we passed recently is a striking example of the former. It shows how unstable the new order is. It indicates that material progress has been more rapid than the economic and social adjustments that have accompanied it. It emphasizes the need of re-evaluation and reconstruction—socially, politically, economically, and educationally. It suggests that oncoming generations should acquire broader understandings and learn to deal more intelligently with their problems than have those of the immediate past. In this connection the teacher of chemistry as well as those of other fields must make genuine contributions.

Paralleling recent social changes, the schools of the nation have made notable adjustments. They have

* Contribution to a symposium conducted jointly by Section C (Chemistry) and Section Q (Education) of the American Association for the Advancement of Science with the Division of Chemical Education of the American Chemical Society, at Atlantic City, New Jersey, December 29, 1936.

[1] HEDRICK, E. R., "Desirable coöperation between educationists and mathematicians," *Sch. & Soc.*, **36**, 769–77 (1932).

expanded physically to provide for thousands of young people released from industry. The length of popular education has been extended to include the junior-college period in many sections of the country. New types of courses have been introduced in response to the need for broader understanding. Curriculums at the secondary and junior-college levels have been greatly modified and enriched. As a result of deliberate experimentation new types of class organization and improved methods of teaching have developed. From intensive studies carried on in classrooms and laboratories has come a clearer understanding of individual interests, capacities, and needs, and of the problems and difficulties involved in different types of learning. Significant as these developments are, they are slight in comparison with those which must occur in the near future. As Professor Dewey has pointed out repeatedly of late, "education must take on new responsibilities and come to grips with realities which it has passed by as outside its province."[2]

The major task which the schools face today has been forcefully described by the Commission of Seven on State Higher Education in California. "It is the primary and fundamental function of the common school system extending from the earliest years of schooling, through kindergarten, elementary school, junior and senior high-school, and junior college, to educate the citizen for effective participation in all those common understandings and coöperations which are necessary to sustain the best in our complex contemporaneous civilization which is American.

"Our common schools must be dedicated primarily to educating men and women so that they may work and live together more successfully in and through the institutions of a civilization that must be adapted to changing conditions. Failure of citizens to understand many of our current problems and their tragic inability to coöperate in the solution of them constitute one cause that has led to breakdowns in our current civilization."[3] Because of the tremendous influence that science and invention have had in molding contemporary life, the natural sciences must contribute generously to the content of general education and must aid in developing the understandings and habits so much needed today.

As a result of the various factors and conditions which have been described, it has been very difficult during recent years to secure a sufficient number of teachers adequately prepared to provide instruction of the breadth and quality desired. The seriousness of this situation was emphasized vigorously by a committee of the Association of American Universities in a recent report on the preparation of teachers. "It is well known that communities have often tolerated teaching of a low level in their overcrowded secondary schools because they were unable or unwilling to incur the expenditures necessary to attract into their employ well-prepared teachers. Added to the difficulties resulting from the pressure of numbers are the problems which have arisen because of the expansion of the curriculum. The secondary schools of the United States have attempted to provide pupils with subjects suited to their diverse needs in preparing for a great variety of vocational and professional careers. The range of subjects covered in the secondary-school curriculum in recent years has been wide, and many teachers have been called on to teach a number of subjects, for some of which they have had little preparation. The assignment of teachers to classes in subjects in which they have deficient preparation is especially frequent in high schools having small enrolments and correspondingly small faculties. A small high school must cope with the complex problems of instruction by requiring each member of the faculty to teach several subjects. Since the majority of the high schools in the United States are small the difficulty here under consideration is general and serious."[4]

The foregoing discussion suggests the urgent need of programs for teachers that will prepare them to meet effectively the challenging responsibilities which social needs and the practical demands of the school impose upon them. Studies made recently by various committees and agencies have led almost universally to the conclusion that the first requisite of an adequately prepared teacher is a broad general education that is directed toward sound scholarship and a cultural background in the major areas of human experience and activity, such as the social sciences, the natural sciences, and the humanities. Among other things it should provide a clear understanding and an appreciation of what each has contributed to civilization and is contributing today to the solution of personal and social problems. Because this phase of the teacher's preparation is often sadly neglected, or indeed omitted, I wish to consider its nature and scope somewhat more fully.

Of large importance is a clear recognition of the various social institutions that affect modern life and of the social, political, economic, and industrial forces operating in this and other countries. Nor should the teacher of any subject be ignorant of the part that such forces are playing in directing the course of human events today. With social understanding should come a social point of view—an attitude of inquiry concerning current change. What things affect human thought and action? Are the changes which are occurring today socially good? How the individual, the potential citizen, and the prospective teacher answers such ques-

[2] DEWEY, JOHN, "America needs an entirely new educational system," *Sch. Management*, **1**, 12 (1932).

[3] "State higher education in California," Report of the Carnegie Foundation for the Advancement of Teaching, June 24, 1932, pp. 17–8.

[4] "Report of the committee on program for graduate study which institutions of higher education should organize for the preparation of secondary school teacher," JOURNAL OF PROCEEDINGS AND ADDRESSES OF THE 38TH ANNUAL CONFERENCE OF THE ASSOCIATION OF AMERICAN UNIVERSITIES, University of Chicago Press, Chicago, **1936**, p. 42.

tions is determined by how well he has come to know and appreciate (*a*) the part played by our great institutions in building up and preserving essential elements in culture and civilization; (*b*) the basic principles underlying social progress; (*c*) the purpose and influence of political and social organizations; and (*d*) the qualities of character essential for good citizenship.

All teachers should be familiar also with the physical and biological world in which they live and with the contributions which the natural sciences have made to social progress and to current habits and standards of living. Their presentation should be made inviting and fascinating in order that deep appreciations may accompany fundamental understandings. A survey of their development should give the student a panoramic picture of the successive stages of scientific knowledge and thought. In harmony with the major purposes of general education, the student should be concerned largely with the humanistic bearings of his findings rather than merely with the impersonal, logical relationships of the facts apprehended. In addition, the disciplinary values of the sciences should be clearly recognized and appropriate training provided.

To the foregoing values of the natural sciences chemistry makes very definite contributions. As Professor B. S. Hopkins pointed out last year at the joint meeting of the organizations which are represented here today, chemistry demands of its students "a carefully trained memory, the ability to observe thoughtfully and intelligently, the power to discriminate between vital facts and non-essentials, and. . . .the skill to interpret the significance of phenomena and to apply new knowledge to useful ends."[5] Certainly these attitudes and habits merit vigorous emphasis if the training provided promotes well-disciplined minds. In addition Professor Hopkins emphasized at length the cultural value of chemistry in general education—its contributions to human progress and to the solution of puzzling contemporary problems. Unfortunately, however, very few high-school and junior-college teachers are sufficiently familiar with this phase of chemistry to provide young people with essential understandings and insights. Consequently chemistry is taught far too frequently for its training values only, or as a body of information to be memorized.

A third area of general education which is highly important for all teachers comprises the humanities. From extensive contacts with the field of literature the teacher should attain such outcomes as a wide acquaintance with the finest ideals of the great minds of all nations; a general knowledge of the accepted writers in the field of history, science, and fiction; the habit of reading and interpreting various kinds of current literature; some technical competence in writing; varied recreational interests in reading; and the habit of finding in literature ideas and ideals of value in stimulating and guiding youth.

A part of the teacher's general training should be devoted to a study of music and art. The contacts provided should insure an acquaintance with and an appreciation of music and art of such nature as to develop desirable understandings and interests, and esthetic tastes and standards. Furthermore, our culture rests on certain basic principles which are revealed in the fields of philosophy, religion, and ethics. A teacher, therefore, who cannot evaluate particular experiences in terms of these general principles is not likely to have a clear grasp of the desirable outcomes of teaching. A survey of philosophical and religious thought should result in such outcomes as an acquaintance with the basic ideas underlying representative philosophies; a knowledge of what the "good life" is, and what roads lead to it; a personal philosophy which is reflected in a wholesome and influential personality; an appreciation of religious and ethical concepts and their basic contributions to civilization; a religious attitude that does not clash with the views of the community; and a functioning idealism that reveals itself in everyday living.

The foregoing requirements are comprehensive and exacting. In most particulars, the outcomes suggested are highly desirable today for all potential citizens. There is general agreement among authorities that the content and scope of general education for teachers differs very little, if any, from that for all well-educated citizens. In the case of teachers, however, an adequate general education has special significance. Its objectives and content are similar to those toward which secondary education is now directed. It is indispensable, therefore, for those who are charged with the responsibility of helping children and young people to similar acquirements. Inasmuch as the present generation of high-school graduates have only partially attained the understandings, appreciations, and disciplines desired, a considerable part of the first two years of most college courses should be devoted to the extension and enrichment of the general or liberal education of prospective teachers.

In institutions which have adopted the broader program outlined above, an effort is made to define clearly the nature and scope of the general education required and the levels of achievement desired. Furthermore, students are permitted to complete this phase of their preparation as rapidly as their previous training and capacity will permit. In this connection, means are adopted for determining whether students have attained satisfactory levels of achievement before they are permitted to register for advanced work. It is thus possible to limit registrations in specialized curriculums for teachers to those who have made the contacts, acquired the understandings, and developed the attitudes which are expected of all reasonably well-educated people today. We cannot expect less of those who aspire to teach.

A second requisite of a prospective teacher is adequate breadth and depth of scholarship in the field or fields to be taught. In the past specialization has usu-

[5] HOPKINS, B. S., "The cultural value of chemistry in general education," J. CHEM. EDUC., **12**, 418–22 (1935).

ally been interpreted to mean the intensive study of a limited field of knowledge within the boundaries of a single department. All too frequently students have followed the same sequence independent of the use they planned to make of their training. An argument often advanced in favor of this type of specialization is that it provides opportunity for pupils to penetrate deeply into a given field, thus insuring a high degree of mastery and insight. Unfortunately, students who specialize narrowly often fail to interpret broadly what they learn, to see significant relationships between the facts acquired and other areas of learning, and to understand the application of their findings to contemporary problems.

During the last few years, however, new meaning and significance has been attached to the term specialization. Increasingly of late it implies breadth of understanding as well as depth of penetration. Some degree of breadth is assured in many institutions which recognize the demand that all teachers should have a reasonably broad and well-balanced general education prior to specialization. If the prospective teacher of chemistry has had such training, he is prepared to begin his specialization on a much broader base than otherwise. In this connection a practical suggestion is pertinent. Departments of chemistry should scrutinize the attainments of prospective teachers who wish to specialize in their departments to determine if they have acquired the understandings, insights, and disciplines in the field of chemistry which should be acquired by all well-educated people. If students do not possess them they should be asked to take the necessary steps either before admission to specialization, or shortly thereafter.

For those who have an adequate background the contacts provided in each field should be such as to promote sound scholarship in the field of chemistry, including a knowledge of its basic facts, concepts, and principles, an understanding of its relationships to the field of knowledge as a whole and to related fields, a critical attitude toward its fundamental theories and philosophies, a clear recognition of its disciplines and skills and reasonable proficiency in their use. The foregoing statements recognize that chemistry, as well as other important fields of learning, has "its own body of ideas, its own logic of organization, its own springs of human interest, and its own processes of growth and expansion."[6] It is highly desirable in my judgment that students should pursue certain phases of chemistry to the frontiers, should see knowledge in the process of making, should feel "something of the glow of intellectual discovery and creation, and be inspired to engage in such pursuits."[6] These experiences are essential if students acquire the interests and understandings which enable them to follow developments in the field, to understand the significance of new discoveries, and to interpret such findings truthfully to others.

The total program of training provided should ensure a broad acquaintance with the sources of information relating to various phases and applications of chemistry and should promote efficiency in the discovery, organization, and interpretation of facts relating to both practical and theoretical problems in the field. Such technics are of major importance in revising and expanding curriculums at the secondary-school level. Experience shows conclusively that only as teachers are able to contribute continuously to the modification and expansion of the curriculum does instruction rise to increasing levels of excellence. Unfortunately, a large majority of teachers are slaves to the information provided in the textbooks used. They have never acquired the intellectual independence or the habits which are essential in moving freely from one area of a field to another or in reorganizing information in terms of a new problem. The difficulties which have been encountered recently in developing broad courses at the junior-college level show that genuine problems are involved. The reconstruction of curriculums in the lower schools requires the use of similar methods of research and interpretation. Unfortunately, very little has been done in most institutions to prepare teachers to assume such responsibilities intelligently. As indicated earlier, the necessary command of a field and the intellectual independence essential in a flexible treatment of its elements are the products primarily of the training and discipline which a department provides.

As implied by the foregoing comments, the need is urgent today for a deliberate consideration by all departments of the breadth and depth of specialized training essential for teaching in high schools and junior colleges. In harmony with this demand, the department of chemistry in one university recently selected the following specific attainments, among others, to be demonstrated by prospective teachers before recommending them for certificates.

"1. Ability to do reasonably independent work in chemistry.

"2. Ability to utilize the chemistry library efficiently in obtaining information relative to a specific problem, including ability to organize and evaluate such information in a critical manner.

"3. Ability to present material, obtained on the basis expressed in (2), in a clear manner, whether orally, graphically, with demonstrations, or in written English.

"4. Ability to recognize the relationships which exist in the application of chemistry to other closely allied fields.

"5. The ability to recognize the applications of chemistry to our everyday life.

"6. An understanding of the basic principles involved in the organization of chemistry material for teaching purposes, a thorough realization of the dis-

[6] HAGGERTY, M. E., "Whither the teachers colleges in the academic world," *Eighth Yearbook, The American Association of Teachers Colleges*, 1929, 32–44.

tinctive types of pupil experiences by which skill in the use of laboratory methods may be acquired and by which the habits of thought involved in making analytical generalizations may be established, and a realization of the general parallelism between learning and research technics in the field of chemistry."[7]

The foregoing outline may be open to various criticisms which can be corrected in harmony with the results of further study of the needs of prospective teachers of chemistry. It represents a significant step forward because it gives clear recognition to specific needs of teachers of chemistry and emphasizes the need of satisfactory attainments if students wish to be recommended for teaching positions. A complete list of attainments of high validity can be developed only after further study of the following issues: the contributions of chemistry to the field of general education; the understandings, attitudes, habits, and skills essential on the part of an efficient teacher at this level; and the breadth and depth of training essential to ensure real scholarship and continuous growth in the field. Progress toward the definition of satisfactory attainments could be greatly accelerated if a committee representing all the interests involved would make this problem the basis of intensive study in the immediate future.

A closely related problem is concerned with requirements when chemistry is taken as a second teaching field. Professor Gortner and his committee rightly recommended in this connection "that the American Chemical Society go on record as emphatically asserting its belief that a prospective instructor should be required to present evidence of an adequate background in subject-matter courses before he or she is eligible for assignment to teach in that particular subject-matter field in high schools."[8] The further recommendation was also made that "a minimum requirement of courses through organic chemistry (because of its importance in life processes) is essential."[8] It would have been very helpful if the committee had carried its analysis farther and specified both the minimum and the desirable attainments of high-school teachers in the field of chemistry. Such a statement would have served as a valuable guide in advising students who elect chemistry as either a principal or a secondary teaching field. After such standards have been set up heroic means must be adopted to develop a consciousness on the part of counselors and advisors of the requirement in a second teaching field. Conferences with students in several institutions lead me to believe that failure on the part of counselors to keep in mind the various needs of prospective teachers is a greater detriment at present to the adequate preparation of teachers than the excessive requirements by some states of courses in education.

[7] "The preparation of teachers," *Announcements, The University of Chicago, Sessions of 1936–37*, **36**, 46 (1936).

[8] "The high school teaching of chemistry," Report of the American Chemical Society Committee, *Sch. & Soc.*, **43**, 604–6 (1936).

The third requirement of a teacher of chemistry is that he should be well qualified for the professional service that society delegates to him. This statement instantly suggests questions concerning the amount and kind of such preparation. May I indicate at the outset that I am in hearty sympathy with the criticism of the committee of the American Chemical Society to the effect that some states and institutions require an exorbitant number of professional courses of prospective teachers. Not infrequently in the past, students have been assigned to such courses, beginning with the freshman year, and have devoted from a fourth to a third of their time to such work. During the last few years, however, three distinct trends have developed. First, the amount of time devoted to strictly professional courses has been reduced in many institutions in response to the urgent demand for greater breadth and depth of training in subject-matter fields. Second, the time of introducing professional courses into the student's program has been postponed considerably as a result of the recognized need for a broad background before such studies are undertaken.

The third trend relates to the effort which has been made in many institutions to define with great precision the nature of the professional training required by teachers at the secondary and junior-college levels. May I illustrate by referring to the steps taken by a committee in one institution. The problem which the committee set for itself was defined as follows: (1) to develop a professional sequence of sufficient breadth to give prospective teachers such an understanding of their problems as was needed and could be provided economically before entering the profession; (2) to provide such a sequence in the shortest time possible commensurate with satisfactory results; and (3) to organize the courses required into a progressive sequence with no unnecessary duplications. As a result of study and experimentation extending over a period of six years, the Committee, and in turn the institution involved, reached the conclusion that an introductory study of professional problems (preceding special methods and practice teaching) may be completed in two courses of three and a third semester hours each. The first is entitled "An Introduction to the Study of Education" and is planned to give the student a clear understanding of the American school system and its social relations and implications, and of classroom organization, management, and control. The second is entitled "Educational Psychology" which aims to acquaint students with the contributions of this field to an understanding of the pupil and the processes involved in learning. It is believed that through careful selection and presentation of materials these two courses, if presented at the senior-college or graduate level, will prepare adequately for the intensive study of the problems involved in teaching specific subjects, such as chemistry.

The adoption of this plan delegates large responsibility for the professional training of teachers to so-called special-methods instructors. The work offered

should be based upon the introductory courses already described and should proceed without duplication of content to studies of the educational problems involved in teaching the subject at the high-school and junior-college levels. It should also follow or supplement a scholarly study of the subject or field involved. This procedure is at variance with the practice of some institutions which provide so-called professionalized subject-matter courses. The validity of the plan here proposed lies in the fact that each subject or field has its own logic and relationships which merit major consideration when subject-matter courses are taken. Furthermore, a student is prepared to consider the problem of organizing and vitalizing instruction at the level of general education only after he has studied a field broadly and is thoroughly familiar with its possibilities and relationships.

The type of special methods course recommended in this report differs from traditional practice in another important respect. Instead of providing a separate professional course for each segment of a field, such as botany, zoölogy, biology, general science, physics, and chemistry, only one course is offered for the field of science as a whole. Experience shows clearly that the principles involved in teaching closely related subjects are similar and that the problems of teaching a given science in a modern high school cannot be taught effectively without an intimate knowledge of the entire science curriculum. Similar statements may be made with respect to other fields. By providing special methods courses based on broad fields rather than specific subjects much time and energy are saved for use in other directions.

An additional problem relates to the department or departments responsible for the organization and presentation of special methods courses. In the early history of teacher education in this country both subject-matter and methods were taught by the same instructor. This plan had many advantages. In the course of time, however, the subject matter of each field expanded and became a matter of absorbing, if not exclusive, interest. Furthermore, highly specialized interests developed in the field of methods. As a result the divorce between subject-matter and methods departments became more or less distinct. It is obvious, however, that the problems of organizing and presenting materials in special fields can be solved effectively today only through the coöperative effort of two kinds of specialists. The educational expert, for example, may determine through experimentation the intellectual needs and habits of pupils at given levels in the school. He may also develop technics by which the appropriateness and effectiveness of instruction for specific groups and individuals can be determined. Subject-matter specialists, on the other hand, may select rich materials that satisfy the needs of pupils from the vast resources at their command and help to organize them into illuminating units. Furthermore, they are best qualified by virtue of their training to determine the relationships that should be emphasized in the study of the field. Through the coöperative effort of both types of specialists, rich bodies of material may be adapted to the level of maturity of the pupils for whom it is intended. The responsibility for its presentation and for the direction of practice teaching should be delegated, in my judgment, to a thoroughly qualified member of the subject-matter department or division concerned. This statement implies that he should possess a high degree of scholarship and competence in both his field of specialization and related teaching problems. The additional statement should be made that an intelligent solution of many of the problems relating to the preparation of tea hers of science, or any other field, lies in the establishment of professional divisions within the respective fields.

Many other problems relating to the professional training of teachers should be considered, such as apprentice teaching preceding actual service, more advanced training following the basic preparation which has been described, the cultivation of appropriate professional attitudes, particularly those which lead to continuous critical studies of teaching activities, and the need for coöperation of all higher institutions in the development of the scientific facts and principles which determine efficient teaching. But time will not permit.

In conclusion, may I emphasize again the fact that the schools of tomorrow must be more closely integrated with the changing social order than has been true in the past. This can be achieved successfully only as higher institutions prepare teachers to assume successfully the broader responsibilities that are involved. The foregoing analysis of the types of academic and professional preparation of teachers of chemistry has been intended merely to suggest problems which merit consideration in the development of appropriate curriculums for teachers. The various phases of the curriculums that have been discussed represent centers about which productive study may be organized. Because of the very nature of the problems involved, they can be solved effectively only through the hearty coöperation of subject-matter and professional departments in any institution that attempts to train teachers. Equally important is the fact that the problems should be attacked experimentally with a clear understanding of the broader functions that schools should serve in contemporary life. Only through such means can popular education rise to the breadth and excellence demanded by the changing social order.

FACTORS AFFECTING *the* ACCURACY *of* TRANSFERENCE NUMBER DETERMINATIONS

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THE DETERMINATION of the transference numbers of the ions from the change in concentration at the electrodes as first proposed by Hittorf is usually included in the laboratory course in physical chemistry. The experience in this laboratory over a period of years using the determination of the transference numbers of silver and nitrate ions indicates that students with no previous experience can secure results of reasonable accuracy only when certain factors are carefully controlled.

Among the factors which affect the accuracy of the determination are (1) the composition and physical condition of the electrodes, (2) the type of coulometer employed and the method of measuring the electrolytic deposit, and (3) the source of current and the voltage employed.

It has been customary to conduct the electrolysis between silver electrodes or a combination of a silver anode and a platinum cathode. Sometimes it is the practice to use a copper cathode in a copper nitrate solution, which is prevented as far as possible from diffusing into the solution of silver nitrate around the cathode. There would seem to be little utility and many objections to the latter procedure. Where silver electrodes have been used, various directions for preparing the electrodes, particularly the anode, have been given. Findlay[1] advises the use of a silver rod and directs that it be silver plated, but gives no specific directions as to the method of plating. There would appear to be no reason for plating the electrode if an unstrained unoxidized surface could be had on the original electrode. A close approach to this is found in a silver foil which has been held in the flame until a thin layer of molten silver just flashes across the surface. This is welded to a piece of platinum wire sealed into a glass tube. The platinum lead wire is covered with De Khotinsky cement which prevents reaction on the platinum in preference to reaction on the silver. Such an electrode is easily and cheaply renewed when sufficiently deteriorated by electrolytic corrosion. If foil 0.01 cm. thick is used, about ten determinations can be made before renewal is necessary.

The copper coulometer has been widely recommended for this determination, in spite of the fact that this coulometer is very inaccurate for small densities.[2] It has been found that the current, as measured by the copper coulometer by comparison with an accurate milliammeter is often fifty to sixty per cent. in error, when low current densities are employed. The silver coulometer is very accurate and, in the form employed, not particularly expensive. A piece of silver foil 0.01 cm. thick, 4 × 4 cm., welded to a platinum wire sealed in glass serves as anode. This dips into a fifteen per cent. solution of silver nitrate contained in a platinum dish of 100 cc. capacity to such a depth that the weld is not immersed. The dish rests on a sheet of copper which is connected to the negative terminal of the current source. The deposit at the current employed (0.006–0.007 amp.) consists of minute silver crystals adhering very tenaciously to the platinum dish, provided the dish is free from organic matter and has been recently scoured with platinum sand. Small particles of loose silver dropping from the anode are easily washed out with a stream from a wash bottle, obviating the use of a porous cup surrounding the anode. The results are exceedingly accurate, and this device is to be preferred to the iodine coulometer in which diffusion effects are hard to eliminate.

With an integrating mechanism such as the silver coulometer in series, it is not essential that the current remain absolutely constant and any source of direct current is suitable, provided the voltage is sufficiently high. Using several different units of the ordinary transference apparatus, we have found that a voltage drop of one hundred thirty-five volts across the apparatus will give from 0.006 to 0.007 ampere through $N/20$ silver nitrate. If this be operated for one and one-half hours, the concentration changes are sufficient to give accurate results, and no change in concentration occurs in the middle portion. In this laboratory, a battery of sixty-two storage cells is used as the current source. With so steady a current as is furnished by a large storage battery, the coulometer is unnecessary, since a good milliammeter and an accurate stopwatch afford adequate precision.

The change in concentration occurring in the vicinity of the electrodes is measured by titration with $N/20$ potassium thiocyanate, with ferric alum as the indicator. Each portion is run out separately into a weighing bottle, weighed and then transferred to an Erlenmeyer

[1] FINDLAY, "Practical physical chemistry," Longmans, Green and Co., New York City, 1923.

[2] MATTHEWS AND WARK, *J. Phys. Chem.*, **35**, 2345 (1931).

flask and titrated. A 25-cc. portion of the original solution is also weighed and titrated. The indicator change is sharp and accurate. With care, the titrations should agree to within 0.05 cc. Assuming that the error is of the same sign in both titrations, a difference of 0.009 in the transference number would occur from an error in titration of this magnitude. Inasmuch as the average deviation in Table 1 is approximately the same as the theoretical error, it may be assumed that with considerable care in analysis, results of adequate precision may be secured.

The results obtained by a group of twenty-eight students are shown in Table 1.

TABLE 1

TRANSFERENCE NUMBER OF THE ANION $\frac{v}{u+v}$

Average	*High*	*Low*	*Av. Deviation*
0.527	0.537	0.504	0.0096

The average value is greatly affected by three very poor determinations. More than fifty per cent. of the group obtained the value 0.534.

APPLIED MATHEMATICS *for* CHEMISTS

*I. A MATHEMATICS LABORATORY AND COURSE**

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FOR a long time it has been maintained that an integral part of the preparation of a chemist was training in mathematics. Not as frequently has the emphasis been placed on the *nature* of the mathematical training. In the average chemical curriculum the mathematics has usually been limited to not more than the first course in calculus. This course has generally been designed by and for the mathematics department and not for the preparation of those, including chemists, who must use mathematics in the solution of the problems of their field.

A. Crum Brown, in his Presidential Address to the Chemical Society in 1892, refers to this and states that what is desired and necessary in the training of the chemist "is not the kind of mathematics that boys are usually taught at school; it is not the kind of mathematics that medical and science candidates have to pass at a preliminary or first B.Sc. examination; it is mathematics for use. It bears to what we may call examination mathematics the same sort of relation that French and German for use bear to much of our school French and German, and the way to learn it is to work with it"(*1*).

The late J. W. Hinchley comments, "It is a sad and common experience of a teacher to find a most hopeful student, in the face of complex industrial problems, abandon the mathematical method in favor of the guess work and 'rule of thumb' of his unscientific predecessors."..."The application of mathematics consists in devising and using labor-saving tools by which thought processes can be carried out automatically and yet with full comprehension of the operation performed" (*6*). He goes on to specify the portions of mathematics which are particularly desirable and refers especially to calculus, particularly graphical calculus. He is careful to point out that the "study of the formal calculus is, however, essential" (*6*).

Mellor early recognized the problem involved and in the preface of the first edition of his "Higher Mathematics for Students of Chemistry and Physics" he states, "I have found that the regular textbooks of mathematics rather perplex than assist the chemistry student . . ., for it is not easy to discover the relation which the pure abstractions of formal mathematics bear to the problems which every day confront the student of Nature's laws . . ." (*9*).

The same experience has been had in other fields than chemistry. Steinmetz, in the preface to the first edition of his "Engineering Mathematics," says that he has not only brought together certain branches of mathematics of peculiar importance to the student of electrical engineering, but that he has added thereto "a number of subjects which experience has shown me to be important for the effective and expeditious execution of electrical engineering calculations. Mere theoretical knowledge of mathematics is not sufficient for the engineer, but it must be accompanied by ability to apply it and derive results—to carry out numerical calcula-

* Presented before the Division of Chemical Education at the ninety-second meeting of the A. C. S., Pittsburgh, Pennsylvania, September 11, 1936.

tions." "Thus considerable space has been devoted to the discussion of methods of calculation and the use of curves and their evaluation, and other kindred subjects requisite for effective engineering work" (*10*).

Doherty and Keller, in their recent "Mathematics of Modern Engineering," approach the problem from a slightly different point of view. They state "the purpose of this text is to facilitate the study and use of mathematics with especial reference to its applications in engineering" (*3*). They emphasize a point which is just as pertinent in the field of chemistry as in engineering. "The use of mathematics as a tool in straight thinking is, in the authors' opinion, not all that it should be. The reason for this seems clear. It is not, as is sometimes implied, that mathematics has been poorly taught; it is that engineering teachers do not make use of it after the basic concepts and forms have been reasonably well taught" (*4*). They further mention that "such a book must show the engineering student how to use mathematics—how to reduce the phenomena under observation to mathematical equations, and then how to solve them" (*5*).

Hitchcock and Robinson, in "Differential Equations in Applied Chemistry" have dealt with some of the same problems. This text is based on an annual course given to students of chemical engineering at Massachusetts Institute of Technology and "the purpose of the book is not to teach chemistry, but to teach mathematics in a form readily assimilated by chemists and chemical engineers."..."The practical needs of the chemical engineer are, however, constantly kept in sight. Much emphasis is placed on graphic methods and on numerical work" (*7*).

Daniels, in his "Mathematical Preparation for Physical Chemistry," has recognized the same fundamental problems and attempted to meet them in still a different way. He states "it is because the author has seen so many students struggling against the handicap of an inadequate preparation in mathematics—spending more effort in avoiding mathematics than needs to be spent in learning it—that this book has been written" (*2*). Further he notes, "The ability to state a problem in mathematical language is invaluable, but the mathematical view point and the technique necessary for carrying out the operations come only with earnest practice" (*2*).

Apparently over a long period of time students of mathematics and the sciences have agreed that training in formal mathematics is necessary, but equally necessary, and frequently lacking, is training in the application of mathematics to the quantitative problems of science. This latter point can be resolved into the following sub-points.

1. Accumulation of necessary mathematical knowledge.
2. Instruction and practice in the mathematical formulation of problems.
3. Explicit training and practice in the solution of mathematical problems by
   - (*a*) Analytical methods
   - (*b*) Numerical methods
   - (*c*) Graphical methods (including mechanical methods)

Any program designed to improve the ability of students of chemistry, or any other science, to use mathematics must satisfy these three main points.

The first point, accumulation of necessary mathematical knowledge, can be best handled in the usual well-planned courses in the mathematics department.

The second point, instruction and practice in the mathematical formulation of problems, seems best handled in the department of specialization, which in this case would be the chemistry department, and should be an integral part of the quantitative approach to the phenomena studied. With the criticism of Doherty and Keller (*4*) in mind it is suggested that one reason for the failure of the student in this respect is that chemistry teachers do not make use of mathematics as a tool in straight thinking after the basic concepts and forms have been reasonably well taught by the mathematics department.

The third point, explicit training and practice in the solution of mathematical problems by analytical, numerical, and graphical methods, can best be handled in a course given in the mathematics department under the direction of that department but with the problem material supplied by other departments, such as the chemistry department.

A course has been designed to accomplish this last point and, for lack of a better name it has been called "Mathematics Laboratory" and the place in which the course has been given has been designated the mathematics laboratory.

The purpose of this course is to give the student insight into and training in the mathematical technics available for analyzing numerical data and practice in the numerical solution of fairly involved problems. There is secondary emphasis on the mathematical formulation of the problem and primary emphasis on the procedure from original data to final numerical results by either analytical, numerical, or graphical methods, or a combination thereof.

The course is a four-hour one-semester course with two class hours per week and two three-hour sessions in the laboratory per week. The course is given in the second semester of the junior year and is taken by students majoring in chemistry, physics, and mathematics each of whom has had at least eight hours in calculus and many of whom have had an additional four-hour course in differential equations. Nine major points are treated during the semester.

The first section deals with logarithms, the slide-rule, and methods of calculation. The emphasis is placed upon logarithms as they occur in formulas, with particular emphasis on logarithms of numbers between zero and one. The recommended slide-rule is the ordinary ten-inch log-log rule. During the remainder of the

term these two mathematical instruments are used whenever possible.

The second section deals with the critical examination of data, averaging, precision of data, the determination of probable errors, and the bases for the rejection of observations.

The third section deals with the problems of plotting data and such associated problems as choice of paper, choice of scale, choice of color of ink, and the additional problem of reproduction of plots. For the remainder of the term frequent use is made not only of rectangular coördinates but also logarithmic and semilogarithmic coördinates, and occasionally of probability paper.

The fourth section deals with empirical equations and the associated problem of the evaluation of constants in rational formulas. In dealing with this subject we use a combination of the graphical-intuitional method.

The fifth section deals with the problems associated with the smoothing of data, with particular emphasis on the philosophical basis for the operation and graphical and numerical methods for performing it. This section is used as an introduction to the following section.

The sixth section deals with the problems and methods of interpolation.

The seventh section deals with the problems associated with the differentiation of a function defined only by tabulated data or by a curve. In dealing with this subject practice is obtained in a variety of methods, including analytical, numerical, graphical, and mechanical differentiation.

The eighth section deals with the problems associated with the integration of a function defined only by tabulated data, or by a curve, and practice is provided in analytical, numerical, graphical, and mechanical integration.

The ninth section deals with the solution of differential equations, particularly those forms that cannot be handled directly by analytical methods.

It is a little difficult to say that a textbook is used in this course, although the students are asked to buy Lipka's "Graphical and Mechanical Computations" (*8*). The laboratory is supplied with a selection of text and reference books dealing with these and related subjects and frequent reference is made to them. Among these books are included:

Daniels, "Mathematical Preparation for Physical Chemistry"
Doherty and Keller, "Mathematics of Modern Engineering"
Goodwin, "Precision of Measurements"
Hitchcock and Robinson, "Differential Equations in Applied Chemistry"
Lindow, "Numerische Infinitesimalrechnung"
Mellor, "Higher Mathematics for Students of Chemistry and Physics"
Running, "Empirical Formulas"
Running, "Graphical Mathematics"
Scarborough, "Numerical Mathematical Analysis"
Steinmetz, "Engineering Mathematics"
Sweet, "Construction of Alignment Charts"
Whittaker and Robinson, "The Calculus of Observations"
Willers, "Methoden der Praktischen Analysis"

and an assortment of mathematical tables, logarithmic and otherwise.

The laboratory is a fair-sized room equipped for the purpose. It is shared by the course in mathematics of statistics. The equipment consists of large flat-topped tables which will seat approximately twelve students at one time, allowing ample space for numerical and graphical work; a blackboard along one side of the room; a commodious storage cabinet for apparatus and supplies at one end of the room; and a large tilting drawing table. The room may be entered directly from the main corridor. It is immediately adjacent to a classroom assigned to the mathematics department, which may be entered through a connecting door. Additional equipment consists of an assortment of triangles, T-squares, straight-edges, French curves, and ship-curves. The department possesses a Bausch and Lomb tangent meter, a Brown and Sharpe movable-blade protractor and a good compensating planimeter. There are available two small hand-operated adding machines and two electric Monroe calculating machines, one a small, old model and the other a ten-key model with automatic multiplication and division.

The course is now entering upon its third year, the assortment of problems used and the methods of presentation followed varying from year to year in the light of experience. The course has proved of interest to a number of those taking it and seems to fill a need in the mathematical training, not only of those who are majoring in mathematics but particularly of those who are interested in other fields, especially chemistry.

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The YOUNG CHEMIST *and the* GOVERNMENT SERVICE

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EVERY student who intends to make chemistry his life work should know that one of the most important fields of employment for the chemist, whatever his specialty, is the civil service. The United States Government employs about one thousand men and women who specialize in chemistry. No subdivision of that great science escapes investigation in one or more of the government laboratories, and the products of the labor of these scientific men and women have enhanced the standard of living of our nation, provided us with wholesome unadulterated food, raised the standard of the public health, improved the quality of the clothes we wear and the innumerable articles we buy, safeguarded the water we drink, and, in certain industrial sections of our country, cleansed the very air we breathe. Our nation's investment in science has drawn and is drawing its full dividends in the betterment of the welfare of its inhabitants.

The Civil Service Commission of the United States has sought to interest chemists in government service. Examinations for the position of Junior Chemist were held each year for students who majored in chemistry. Some interesting figures concerning recent examinations for Junior Chemist are included in Table 1.

TABLE 1

Year Ending June 30th of	*Number Examined*		*Number Passed*		*Number Appointed*	
	Male	*Female*	*Male*	*Female*	*Male*	*Female*
1924	104	18	54	2	20	0
1925	193	38	87	11	30	0
1926	269	31	133	5	35	1
1927	224	45	120	17	48	3
1928	261	32	106	8	54	3
1929	357	58	201	24	70	3
1930	425	69	151	15	69	3
1931	1030	143	462	63	44	1

In the interval from 1931 to 1935, the eligible lists of chemists were so ample, and appointments so few, that the government did not deem it desirable to hold further Junior Chemist examinations. In 1936, however, an examination was held. Figures regarding the examination are not available, but it is believed to have attracted several thousand candidates.

A study of the above figures permits certain conclusions. During the years before the business depression, the number of candidates taking the Junior Chemist examination, while varying considerably, averaged but two hundred forty-three per year for the period from 1924 to 1928 inclusive. During the depression, however, the number of candidates presenting themselves for examination increased by leaps and bounds, the average for the years 1929 through 1931 inclusive being six hundred ninety-four. This quickening of interest in Civil Service positions during periods of depressed industrial activities is very characteristic. In this connection, it can be pointed out that in 1925, the Assistant Chemist examination was taken by fifty-five chemists. Ten years later, in 1935, the same examination attracted 1836 chemists.

During the period covered by the above figures, there appears to be no significant variation regarding the proportion of candidates to pass the examination. The poorest showing was, in the case of men, in 1930 when thirty-six per cent. passed; and in the case of women in 1924, when eleven per cent. passed. In 1925, the proportion of men to pass reached its highest of fifty-six per cent. and the proportion for women reached its highest of forty-four per cent. in 1931. In each year, the percentage of failures was greater among women than among men. This furnishes perhaps an additional argument (if another one is required) as to why women should seek their careers in marriage and not in chemistry. Of those men who passed the examination, fifty-one per cent. received appointments in 1928 as against 9.5 per cent. in 1931. The corresponding percentages for women are thirty-eight per cent. in 1928 and none in 1924. As stated before, the policy of the Civil Service Commission of giving a Junior Chemist examination was resumed in 1936 after a lapse of four years. And with the apparent betterment of our economic life, the custom of giving the examination each year may be resumed.

The examination is a written one and consists of two parts. The first part, in general chemistry and elementary physics, is required of all candidates. For the second part, the student may elect to take one or, if he chooses, two of the following subjects; organic, inorganic, physical, analytical, or physiological chemistry. Separate lists of eligibles are made up from each of these examinations. The observer of Civil Service matters cannot fail to be impressed by the impartiality of the proceeding. The candidate is warned in his application form to avoid reference to religion, politics, or fraternal orders. The examiner who rates the candidate's paper knows him only by number.

The writer received his appointment from the eligible list in analytical chemistry. The work consists in the analysis of a wide variety of materials to determine their compliance with the specification requirements. For instance, the type of spaghetti that is purchased by

the Navy Department must have an ash content of not more than 0.65 per cent., moisture less than twelve per cent., and protein at least eleven per cent. Baking powder has definite requirements for aluminum, phosphorus, and available carbon dioxide. The imitation vanilla flavor purchased by the Navy must contain at least 0.1 g. of coumarin, 0.6 g. of vanillin, and 35 cc. of glycerol per 100 cc. of the product. Vegetable shortening should have an iodine number of less than 75. Canned sausage may contain not more than four times as much moisture as protein. Crude fiber in cocoa must not be over seven per cent., calculated on a fat and moisture-free basis. Gold lace must contain at least two per cent. gold and ninety per cent. silver. Silk neckerchiefs must not be too heavily weighted. Cotton fabrics must be free from artificial sizing, such as starch; wool-cotton mixtures must contain a definite percentage of wool. Tableware should contain at least eighteen per cent. nickel. The acid number of white floating soap must be not less than 212 and so on.

The work is thus seen to be of a rather strict analytical nature, although there is plenty of room for ingenuity and research ability as applied to the improvement of methods of analysis. The preparation of accurately standardized solutions of acids, alkali, silver nitrate, ammonium thiocyanate, sodium thiosulfate, etc., is of course a necessary part of the procedure. If the quantity of this work is insufficient to keep a chemist busy for eight hours of each working day, there is other work of a very routine nature to do, but a tenaciously lingering sense of professional pride forbids the writer to enumerate these routine tasks.

The first appointment which the Junior Chemist receives is likely to play an important rôle in his career. Transfers are rather difficult to obtain and many a chemist has reached the retirement age in the laboratory where, as a young man, he first began his work. Thus, if the first appointment is to a research laboratory, located in a city where opportunities for graduate study are available, the young chemist can well develop into a recognized specialist in his particular field.

Most of the research laboratories, though by no means all of them, are located in Washington, D. C. This city is very favorably situated from an educational standpoint. The local universities conduct special late afternoon and evening sessions for government workers and it is entirely possible for a young man to win his Ph.D. degree by attending these classes after working hours. Although possible, it is an achievement of great difficulty; a task not to be essayed by those timid souls who would let, "I dare not wait upon I would." Some government departments, like the Department of Agriculture, give courses to their younger scientific workers which are accredited by the local universities.

The Department of Agriculture employs more chemists than any other in our government. Its vast organization is divided into bureaus under which widely diversified and important researches are conducted. The Bureau of Animal Industry is primarily concerned with the protection and development of the livestock and meat industries of the United States. It deals with problems concerning the feeding of animals and also the nutritive value of the different animal foods eaten by man. It attempts to control or eradicate diseases of livestock. It is charged with the enforcement of federal laws relating to the meat industry.

The Bureau of Dairy Industry conducts researches of a fundamental nature concerning the nutrition of dairy cows and the manufacture of dairy products. The work involves chemistry and bacteriology. The organic chemist, for instance, studies milk powder, evaporated milk, the oxidation of fats in the deterioration of butter, and the heat stability of ordinary milk; all problems of far-reaching importance.

The Food and Drug Administration, employing more than one hundred fifty chemists, is charged with the enforcement of those comprehensive acts of Congress designed to safeguard the quality of our food and drink. Many new methods of analysis have been developed by this bureau. These are written into the specifications of the particular products which they concern. The methods they employ to standardize foodstuffs are chemical, pharmacological, bacteriological, and microscopical. Despite limitations that are inherent in the Food and Drugs Act itself, the Administration has succeeded in giving the American public a food supply that is probably unsurpassed anywhere in the world. Canned lobster as well as evaporated milk, jam as well as cocoa, all engage their attention. The Food and Drug Administration is also responsible for ensuring that the medicines and drugs sold to the public are of standard quality, unadulterated, and not misbranded. Their inspectors who investigate the processes of manufacture in the food and drug trades are frequently taken from the civil service lists of eligible chemists.

The Forest Service, another important bureau of the department, has its research laboratory located in Madison, Wisconsin. The work there involves theoretical and practical scientific studies in the chemistry of pulp and paper manufacture, glue, wood preservatives, and paint application. The work is carried out in coöperation with the University of Wisconsin, and the chemists there are afforded an excellent opportunity for graduate work. They may receive university credit for work done in the government laboratory. The underlying aim of this Service is to utilize to the utmost the resources of our immense national forests.

The Bureau of Plant Industry, as its name indicates, is devoted to plant research and related problems. Men who received their early training in organic and physiological chemistry have entered the field of plant physiology, and have found their chemical training to be of fundamental importance to them in their work. The researches of this bureau on plant diseases and methods of eradication and control have found vast practical application. A great deal of pioneer work on the important problem of the relationship of light to plant growth was done by a plant physiologist whose

early training was in the field of chemistry. A valuable adjunct to the work of this bureau is the experimental farm which it maintains at Arlington, Virginia, near the District of Columbia.

The Bureau of Home Economics is a stronghold of the woman chemist. The important field of vitamin research as a part of general nutrition receives the attention it merits in this bureau. The chemists there also study the composition and properties of textile fabrics of cotton, wool, and other fibers, and the effects of reagents, used in the household, on these materials.

The Bureau of Plant Quarantine is charged with the difficult task of preventing the entry of plant pests into the United States. Those that have gained a foothold here, the Bureau attempts to restrict by throwing around them a "cordon sanitaire." This bureau employs relatively few chemists, the work being done in the main by entomologists and plant quarantine inspectors.

The division of the Department of Agriculture which employs more chemists than any other, is the Bureau of Chemistry and Soils. Its fine research organization studies, among other things, foods and their physiological effects on the human organism; the utilization of the raw materials of the farm; the means of prevention of dust explosions; and the manufacture of fertilizers, a problem which includes the study of nitrogen and its fixation.

Another department of the government which employs chemists is the Department of Commerce whose Bureau of Standards is known the world over for the precision and elegance of its work. About one hundred chemists serve in this great institution. Other departments employing chemists are the Department of the Interior with its Geological Survey Division, the Navy Department with its Bureau of Supplies and Accounts, the Treasury Department which controls the Public Health Service and the War Department.

According to the official specifications for the position of Junior Chemist, he is called upon "To assist chemists of higher grade by performing routine steps in chemical research requiring fundamental technical training but not involving the necessity for mature judgment, the responsibilities for interpretation of data, or the authority to make recommendations on the basis thereof." He may be called upon to perform a great variety of chemical analyses, most of which are in accordance with standard laboratory methods.

The entrance salary for the Junior Chemist is $2000 per year. He can win promotion through the grades to Assistant Chemist, Associate Chemist, Chemist, Senior Chemist, Principal Chemist, and Head Chemist. The latter position commands a salary of about $7500 per year. It must be said, however, that in the last five or six years, promotions have been rare. The few Head Chemists in the government service are all outstanding in their profession. The one in the Public Health Service, for instance, is a Willard Gibbs medalist; the one in the Navy Department is an associate editor of "International Critical Tables." Although the writer has no statistics to fortify his assertion, he feels it safe to say that of those chemists who enter the government service, themselves selected men, not more than one per cent. rise to the rank of head chemist. Thus do the stern eliminative processes of life in the course of time gradually assert themselves. "Many are called, but few are chosen." Service with the government carries with it the decided advantages of steady employment, opportunity for graduate study, annual leave with pay, sick leave, and provision for retirement. Thus it is not difficult to see why many chemists seek to make their careers in government service.

The criteria defining the different grades of chemists are based primarily upon the differences in the duties and responsibilities of the work, and on the experience requirements. Thus while the Junior Chemist is supposed to work "under immediate supervision and with little opportunity for independent or unreviewed action or decision," the Assistant Chemist works "under general supervision, with limited latitude for independent or unreviewed action or decision." The quotations are taken from the official government publication entitled, "Preliminary Class Specifications of Positions in the Field Service." A candidate for the position of Junior Chemist has to be a graduate of a recognized college and must have majored in chemistry. A candidate for Assistant Chemist must fulfil that requirement and in addition must have had at least two years of graduate work or two years of acceptable experience.

It is not to be denied that a significant section of the American public holds the opinion that government positions generally are manned by incompetents whose work is characterized by inefficiency. This opinion, fraught with so much mischief to the public good, rests upon a misconception that is easily uncovered. The misconception is that this section of the American public has grouped all government employees in one category, whereas they should be divided into two broad classes. The first class includes those who have obtained their positions by virtue of their social position, wealth, membership in fraternal orders, religious affiliations, political preferment, or similar reasons. The second group comprises those who having passed competitive civil service examinations, and, having complied with all other requirements of the civil service, have received appointments. With those who fall within the first group, this discussion is not concerned. Regarding the second group, the voluntary utterances of private personnel experts can be invoked, testifying to the efficiency, the loyalty, the general competence of the true civil servant. It is upon this latter group that there rests, in great measure, the responsibility for the immense task of conducting the business of government.

The writer will now venture a few words of advice, offered in the friendliest and most cordial spirit, to those students who contemplate taking the Junior

Chemist examination. Concentrate on one of the optional subjects and do not try to take the examination in two of them. A very high grade in the examination in general chemistry and one of the optionals is infinitely preferable to a merely passing grade in two of the optional subjects. The choice appointments, those offering the finest opportunities, are given to the men at the top of the list. They are the appointments worth getting and worth striving for. Then, when you have received your appointment, allow free play to all your intelligence, industry, diligence, resourcefulness, personality—and luck.

SULFURIC ACID BY THE LEAD CHAMBER PROCESS. A LABORATORY EXPERIMENT

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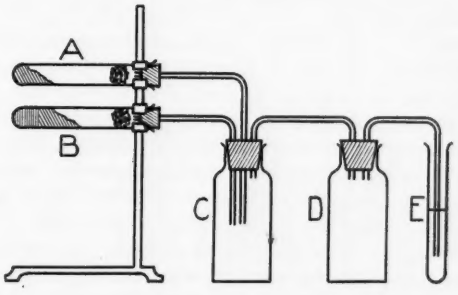
INDUSTRIAL processes usually cannot be reproduced by students in elementary chemistry laboratories. In most courses such processes are illustrated as often as is feasible by lecture demonstrations which involve more or less complicated setups. It is questionable in these cases whether the student absorbs much in the way of experimental technic or of the basic principles involved. It would seem, then, that any experiment which allows reasonable reproduction of an important industrial process by the student in the laboratory should be of interest to teachers of elementary chemistry.

The preparation of sulfuric acid by the lead chamber process is the subject for a lecture demonstration in many elementary chemistry courses. Several years ago Billinger[1] outlined a method of preparing sulfuric acid, this method being suitable for use by advanced students in elementary chemistry laboratories. The purpose of the present article is to outline a modification of this experiment which makes it safe to use in any beginning chemistry laboratory, and which at the same time involves no apparatus more complicated than wide-mouth bottles and test-tubes.

In the chamber process sulfuric acid is produced from sulfur dioxide, oxygen, and water, using oxides of nitrogen as catalysts. Tube *A* in the accompanying diagram contains five grams of copper nitrate crystals which, when heated, yield the water, oxygen, and oxides of nitrogen. Tube *B* contains a mixture of five grams of finely ground sulfur and ten grams of powdered manganese dioxide, upon which has been poured an additional ten grams of the latter material. Plugs of glass wool are placed in these generators between the charges and the delivery tubes. These, together with the layer of manganese dioxide in tube *B*, prevent plugging, which was a serious drawback in the earlier method. The exit tubes from the gas generators should extend about half-way into the reaction bottle *C*. Extension to the bottom causes the majority of the chamber crystals to form directly under the tubes, where they are not so easily observed by the student as when they are formed on the sides. Bottle *D* is a safety trap which prevents liquid in *E* from sucking back into *C*. *E* represents a test-tube partly filled with concentrated sulfuric acid and fulfils the same purpose as that of the Gay-Lussac tower in commercial plants.

The experiment is carried out by gently heating the generator tubes with a Bunsen burner until steam, nitrogen dioxide, and sulfur dioxide pour into the reaction flask. Best results are achieved if an excess of nitrogen dioxide is maintained during the entire process. This excess is easily recognized by the characteristic brown color of the gas. In a short time the reaction bottle becomes coated with white "chamber crystals." Heating is then discontinued, the reaction bottle is removed,



and sufficient water is added to dissolve the crystals with the resulting formation of sulfuric acid.

The whole procedure, including the setting up of the apparatus, may be easily carried out by a student in a two-hour laboratory period. The quantity of sulfuric acid formed is large enough to allow for tests and further experimentation. The experiment as outlined has been tried out in the beginning laboratory course in chemistry at Lehigh University and found to be quite satisfactory. Ordinary seven-inch Pyrex test-tubes were used for the gas generators, but soft glass test-tubes may be substituted. The reaction and safety bottles were standard eight-ounce wide-mouth bottles.

[1] BILLINGER, R. D., "Nitrosyl-sulfuric acid: an experiment illustrating the lead chamber reaction," J. CHEM. EDUC., 7, 1138 (May, 1930).

EXPERIMENTS *on the* REACTIVITY *of* ORGANIC COMPOUNDS *for an* INTRODUCTORY COURSE *in* ORGANIC CHEMISTRY*

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THE difficulties with which the beginner in organic chemistry is faced are tremendous. Bewildering accumulation of facts with but few correlating principles contrives to confuse the relations between the vast number of organic compounds. Most of the work of the beginner in the laboratory is not particularly helpful toward correlating the reactions even of compounds of the same group, because the experiments are almost entirely preparation experiments. A typical compound is usually prepared by a general method which is applicable to the preparation of other members of the same group, and a few of the constants of the compound, such as boiling point, or melting point and solubility, are determined. Occasionally, a characteristic reaction of the compound with a common reagent is appended at the end. For example, an examination of five texts on laboratory experiments in organic chemistry disclosed that on the study of the alkyl monohalides the experiments consist of the preparation of ethyl iodide or *n*-butyl bromide or both. Moreover, in all these texts the entire work is devoted to the preparation, separation, purification, determination of the boiling point, and recording of the yield. In only one does there appear a single test with a reagent. Perhaps in the beginning the acquisition of technic in the methods used in preparation of organic compounds is very essential, but it is not always necessary to spend the entire time of the laboratory period making or attempting to make one compound after another, which reduces the laboratory practice to mere routine.

For a number of years we have been interested in the development of an introductory course in organic chemistry in which the reactivity of certain groups or radicals is introduced rather early. If organic compounds are represented by the general formula R-X, where R is the organic radical and X the functional group, it is reasonable to assume that trends in the rates of reactions of compounds with a common group X but different radical (R), are an indication of the influence exerted by the structure of the radical. In this attempt, the need was felt for simple experiments which would bring out not only the relations and differences between members of one group and those of another, but also between members of the same group.

A few of these simple experiments are described, as they are believed to be applicable to any class of beginners in organic chemistry.

THE REACTIVITY OF THE MONOHALOGEN COMPOUNDS

The reactivity of the monohalogens is a controversial topic, as in practically all investigations the reactions used for its determination are different. Most investigators employ a reaction which takes place at a measurable rate and permits the determination of the rate constant. The assumption is made that given a particular reactant the rate with which the various members of a particular series of halides react is an indication of the effect of the organic radical R to which the halogen is attached. Of the methods which have been used the following may be mentioned. Wislicenus[1] determined the time required for the halide to react with the sodium derivative of ethyl acetoacetate

$$RI + CH_3COCHNaCOC_2H_5 \longrightarrow CH_3COCH(R)COOC_2H_5 + NaI \quad (1)$$

Hecht, Conrad, and Brückner[2] used the rate of reaction of the halide with sodium ethylate to give ether

$$RI + NaOC_2H_5 \longrightarrow ROC_2H_5 + NaI \quad (2)$$

Menschutkin[3] used the rate of formation of quaternary salts with triethyl amine

$$RI + (C_2H_5)_3N \longrightarrow (C_2H_5)_3NRI \quad (3)$$

Burke and Donnan[4] used the rate of reaction of the halides with silver nitrate dissolved in alcohol, while Segaller[5] used the rate with sodium phenoxide

$$RI + C_6H_5ONa \longrightarrow C_6H_5OR + NaI \quad (4)$$

* Presented at the ninety-second meeting of the A. C. S., Pittsburgh, Pennsylvania, September 10, 1936.

[1] WISLICENUS, *Ann.*, **211**, 239 (1882).
[2] HECHT, CONRAD, AND BRÜCKNER, *Z. physik. Chem.*, **3**, 450 (1889).
[3] MENSCHUTKIN, *Z. physik. Chem.*, **5**, 589 (1890).
[4] BURKE AND DONNAN, *J. Chem. Soc.*, **85**, 555 (1904).
[5] SEGALLER, *ibid.*, **103**, 1154 (1913).

Cox[6] employed sodium α- and β-naphthoxides. Clarke[7] used the reaction of bromides with pyridine in alcohol

$$RCH_2X + C_5H_5N \longrightarrow C_5H_5N\langle \begin{matrix} X \\ CH_2{\cdot}R \end{matrix} \quad (5)$$

Slator[8] used the reaction of iodides with sodium thiosulfate in the presence of alcohol and water

$$RI + Na_2S_2O_3 \longrightarrow RNaS_2O_3 + NaI \quad (6)$$

Conant[9] and his collaborators used rate constants from the metathetical reaction of the chlorides with sodium iodide in acetone

$$RCl + NaI \longrightarrow RI + NaCl \quad (7)$$

Hartel, Meer, and Polyáni[10] employed as a measure of reactivity the reduction of the diameter of the sodium vapor flame when it is burned in presence of organic halides.

Gilman[11] uses as a measure the average time required for development of a characteristic color when certain proportions of the halide, ether, and magnesium are treated with a solution of Michler's ketone. Tronov[12] has used the reactions of halides with sodium methylate, pyridine, and piperidine.

At present, certainly, no satisfactory conclusion can be derived, as the results of the various investigators are not in total agreement. It is possible, however, in the case of the monohalides, to avoid controversial ground, if the reactivity is restricted to the rates of hydrolysis as related to their ease of formation from the monohydroxy compounds. With this restriction a few useful experiments can be developed, and several of these are described, as they are believed to be applicable to a class of beginners.

The general formula for the hydrolysis of the halogen compounds and their preparation from the monohydroxy derivatives is given by the following equation:

$$RX + H_2O \rightleftharpoons ROH + HX$$

If a small amount of halide is added to pure water, hydrolysis will change the hydrogen-ion concentration of such solution. This can be experimentally determined by the pH of the solution. By the addition of a few drops of an indicator with a range of pH 1–13 to the water or solution prior to the addition of the halide, the rate of change can be observed. For example, the compounds listed in Table 1 below are all chlorides but differ vastly in their reactivities.

TABLE 1

COMPARISON OF RATES OF HYDROLYSIS OF SEVERAL HALOGEN COMPOUNDS

(Five cc. of water, 10 drops (0.001–0.002 mole) of the halide and 10 drops of Universal Indicator)

		Approximate pH		
No.	*Chloride*	*Immediately after mixing*	*After five minutes room temp.*	*After heating for 0.5 hr. at 55–60°C.*
1	Pure Water (Blank)	6.0	6.0	6.0–6.5
2	*n*-Butyl Chloride	6.0	6.0	5.0
3	*iso*-Butyl Chloride*	4.0	3.5	2.5
4	*sec.*-Butyl Chloride	6.0	6.0	4.0
5	*tert.*-Butyl Chloride*	3.5	2.8	1.2–1.5
6	*n*-Amyl Chloride	6.0	6.0	5.5
7	*iso*-Amyl Chloride*	5.5	5.0	4.5
8	*n*-Hexyl Chloride	6.0	6.0	5.5
9	Cyclohexyl Chloride	6.0	6.0	5.8
10	Phenyl Chloride (Chlorobenzene)	6.0	6.0	6.0
11	Benzyl Chloride*	4.5	4.0	3.5
12	α-Chloronaphthalene	6.0	6.0	6.0

* These chlorides show more rapid initial hydrolysis as indicated by the change in the pH of the solution.

The addition of ten drops of the chloride (0.001–0.002 mole) to five cc. of water with the proper amount of indicator shows an immediate change in the case of tertiary-butyl chloride, reaching a pH of 3 within five minutes, while benzyl chloride in the same interval has changed to pH 4. The other chlorides do not show any appreciable change. Heating at 55° to 60°C. accelerates the rate of hydrolysis so that at the end of one-half hour it is possible to observe some slight changes even in the less reactive chlorides. The results of the experiment as performed by students are shown in Table 1.

Experimental.—To five cc. of distilled water, add ten drops of Universal Indicator† (with a pH range of 1–13), and ten drops of the halide. Shake the test-tube for ten seconds, and observe the pH of the aqueous layer by comparing with a color chart furnished with the indicator. The tube is then set aside on the rack. Observe the pH again in five minutes. Then immerse all the tubes in a beaker containing water kept at 55° to 60°C. After one-half hour, the pH is again observed. In the last observation, if necessary, add a few more drops of the indicator before making the comparison with the color charts as there is a tendency for the color to pass into the halide layer.

The relative ease of hydrolysis of the chlorides can then be related to the relative ease of formation from the monohydroxy derivative in accordance with equation (1), previously shown. The three butyl chlorides can illustrate this relation as follows:

In each of three large test-tubes place 12 cc. of concentrated hydrochloric acid. To the first add 5 g. of *n*-butyl alcohol, to the second 5 g. of secondary butyl alcohol, and to the third, 5 g. of tertiary butyl alcohol. Shake at intervals for five minutes. If a halide has been formed, it will form a separate layer. Separate the lower layer of those mixtures which have reacted by means of a separatory funnel.

Add 5 g. of zinc chloride to the mixtures that did not react and heat on a water bath for one hour, after first providing the

[6] COX, *J. Chem. Soc.*, **113**, 666, 821 (1918).
[7] CLARKE, *ibid.*, **97**, 416 (1910).
[8] SLATOR AND TWISS, *ibid.*, **95**, 93 (1909).
[9] CONANT AND KIRNER, *J. Am. Chem. Soc.*, **16**, 232 (1924); CONANT AND HASSEY, *ibid.*, **47**, 476 (1925).
[10] HARTEL, MEER, AND POLYÁNI, *Z. physik. Chem.*, **19B**, 139 (1932).
[11] GILMAN AND VANDER WAL, *Bull. soc. chim.*, **45**, 344 (1929).
[12] TRONOV, *J. Russ. Phys.-Chem. Soc.*, **58**, 1278 (1926); *Ber.*, **63B**, 3060 (1930). For a more complete bibliography see *Chem. Reviews*, **16**, 192 (1935).

† Any long-range indicator can be used. The one used in this work is the S. L. C. Universal Indicator supplied by Wilkens-Anderson Co. of Chicago. The color chart which accompanies the indicator shows fifteen colors corresponding to definite pH. Several long-range indicators are described in W. M. CLARK's book, "The determination of hydrogen ions," The Williams & Wilkins Co., Baltimore, Maryland, **1928**, p. 96. See also "Demonstration experiments using universal indicators," by L. S. FOSTER AND I. J. GRUNTFEST, J. CHEM. EDUC., **14**, 274–6 (1937).

tube with a cork through which a glass tube about a foot long serves as an air condenser. Separate the chloride formed, and compare the yields.

The difference in the reactivity of the chlorides, bromides, and iodides can be demonstrated by similar experiments.

Table 2 shows the results obtained using the three normal and three secondary halides.

TABLE 2

COMPARISON OF RATES OF HYDROLYSIS OF SEVERAL BUTYL HALIDES

(Five cc. of water, 10 drops of halide, and 10 drops of Universal Indicator)

		Approximate pH	
No.	*Halide*	*After 15 minutes at room temp.*	*After heating for 0.5 hr. at 55–60°C.*
1	Water (Blank)	6.0	6.5
2	*n*-Butyl Chloride	6.0	5.5
3	*n*-Butyl Bromide	6.0	5.0
4	*n*-Butyl Iodide	6.0	5.5
5	*sec.*-Butyl Chloride	6.0	4.0
6	*sec.*-Butyl Bromide	5.5	3.8
7	*sec.*-Butyl Iodide	5.5	4.0

The matter of solubility of these halides, particularly in the case of bromides and iodides, and the distribution when shaken makes the results merely indicative of the trend.

That the rate of iodides (in the beginning, at least) is faster than that of the chlorides and slightly faster in many instances than those of bromides can be illustrated by using a more sensitive indicator, such as bromothymol blue.

Table 3 shows the results obtained with the secondary halides, with the use of bromothymol blue as the indicator.

TABLE 3

COMPARISON OF THE RATES OF HYDROLYSIS OF *sec.*-BUTYL HALIDES

(Five cc. of water, adjusted to pH 7,* 10 drops of the halide and 10 drops of bromothymol blue 0.04 per cent. solution)

		Approximate pH—Room Temperature				
No.	*Halide*	*After 1 min.*	*After 3 min.*	*After 6 min.*	*After 8 min.*	*After 15 min.*
1	Water (Blank)	7.0	7.0	7.0	7.0	7.0
2	*sec.*-Butyl Chloride	7.0	6.9	6.9	6.8	6.8
3	*sec.*-Butyl Bromide	6.8	6.7	6.5	6.3	6.1
4	*sec.*-Butyl Iodide	6.7	6.6	6.5	6.4	6.3

* To 100 cc. of water, add one drop of 0.1 *N* sodium hydroxide.

The results definitely indicate that in the case of the alkyl halides the iodides are the least stable and, therefore, more reactive, while the chlorides are the most stable and, therefore, least reactive. The uses of the monohalides can be related to these rates. Iodides are used in the laboratory where a greater reactivity is desired, while their use in industry is nearly always prohibitive in cost. The chlorides are used in industry and, therefore, means for accelerating the rate of reaction are employed, such as heating under pressure and in the presence of catalysts. Chlorobenzene which the student found unsuitable for the preparation of phenol is hydrolyzed industrially by heating at 300 atmospheres pressure and at a temperature of 320°C., with a 10 per cent. aqueous sodium carbonate solution in the presence of copper metal as a catalyst.[13] Further, chlorobenzene is aminated to give aniline, by heating with aqueous ammonia under pressure at about 200°C. in presence of copper salts.[14]

THE RATE OF OXIDATION OF MONOHYDROXY COMPOUNDS

It is desirable to illustrate experimentally several points to a class of beginners in connection with the study of alcohols. The student learns on the blackboard or on paper that alcohols are classified as primary, secondary, and tertiary upon the basis of structure, particularly as revealed by their oxidation products. It seems possible that an experiment can be devised to show differences in the rates of oxidation which can be related to their structure.

The primary alcohol is oxidized to an aldehyde, and this, in turn, is easily oxidized to an acid with the same carbon content as the alcohol. The secondary alcohol is oxidized to a ketone and further oxidation involves rupture of carbon-to-carbon linkage; therefore, the oxidation should proceed at a slower initial rate. Finally, the oxidation of the tertiary alcohol involves, from the very beginning of the reaction, the rupture of the carbon-to-carbon bond; consequently, the tertiary alcohol should have the slowest rate. Another point that is desirable to illustrate by a simple experiment is that if the general formula of alcohols is expressed as R-OH, then the rate of oxidation increases with the increase in the length of the chain or introduction of a phenol group. Both these points can be illustrated by adding approximately equal amounts of the various alcohols to 0.03 per cent. neutral potassium permanganate solution and then observing the rate of the change in color of the solution at various intervals.

Table 4 shows the results obtained with the use of various monohydroxy compounds.

TABLE 4

RATE OF OXIDATION OF SEVERAL MONOHYDROXY COMPOUNDS

(Ten drops of the hydroxy compound added to 10 cc. of 0.03 per cent. neutral potassium permanganate solution)

		Color Change	
No.	*Compound*	*Immediately*	*After 10 min. (room temp.)*
1	Methanol	No change	Minimum change
2	Ethanol	No change	Reddish brown
3	Butanol	Red*	Reddish brown
4	*iso*-Butanol	Red*	Reddish brown
5	*sec.*-Butanol	No change	Less than 3*
6	Trimethylcarbinol	No change	No change
7	Cyclohexanol	Red	Red brown
8	Phenol	Brown*	Entirely decolorized
9	Benzyl Alcohol	Immediately Red*	Brown
10	Blank	Purple	Purple

* Monohydroxy compounds which show the most rapid initial rate of oxidation.

Experimental.—To ten cc. of 0.03 per cent. potassium permanganate solution (neutral) add ten drops of the alcohol. Shake for ten seconds, observe the color immediately, and allow to stand at room temperature for five to ten minutes. Observe

[13] GROGGINS, "Unit processes in organic synthesis," McGraw-Hill Book Co., New York City, 1935, p. 572.

[14] *Ibid.*, p. 306.

the color of the solution again in five minutes; then set the tubes in a water bath at 55–60°C., observing at intervals the time required for reduction of the permanganate. The permanganate solution is made by diluting a stock one per cent. solution.

The results from these observations agree qualitatively with the constants obtained by Tronov.[15] The decreasing ease of oxidation of the monohydroxy compounds listed in Table 4 is as follows: phenol, benzyl alcohol, cyclohexanol, butanol and *i*-butanol, *sec.*-butanol, ethanol, methanol, and trimethylcarbinol.

The use of alkaline and acid permanganate with methanol, ethanol, and butanol illustrates more strikingly the difference in the rate of oxidation with increased complexity of the radical. When butanol is mixed with 0.03 per cent. potassium permanganate solution which contains 0.1 *N* hydroxyl-ion concentration, the solution becomes green instantly, due to the reduction of the permanganate to the manganate ion. Ethanol gives the same reaction more slowly, and methanol is slowest of all.

Experimental.—The reaction is performed in the same manner as above. The acid permanganate is prepared by diluting the 1 per cent. stock solution of permanganate to 0.03 per cent., adding sufficient sulfuric acid to bring up the concentration of H^+ to 1 *N*. Similarly, by the addition of sufficient sodium hydroxide to make the OH^- concentration 0.1 *N* the alkaline permanganate is prepared.

Table 5 shows the average results obtained.

TABLE 5

COMPARISON OF THE RATES OF OXIDATION IN NEUTRAL ALKALINE AND ACID PERMANGANATE OF THREE LOWER ALCOHOLS

(Ten drops of the alcohol added to 10 cc. of 0.03% of the permanganate solution)

		Color Changes of Solution at Room Temperature		
No.	*Alcohol*	*0.03% Neutral permanganate*	*0.03% Alkaline permanganate (OH^-) 0.1 N*	*0.03% Acid permanganate (H^+) 1.0 N*
1	Methanol	No change—10 min.	Green—2 min.	Slt. action—10 min.
2	Ethanol	Red in 5 min.	Green—30 sec.	Opaque red—5 min.
3	Butanol	Light red—5 min.	Green—15 sec.	Opaque red—3 min.
4	Blank	Purple	Purple	Purple
		After 10 Minutes Immersed in Bath at 55–60°C.		
1	Methanol	Dark red	Brown precipitate	Decolorized* in 35 min.
2	Ethanol	Red	Brown precipitate	Decolorized* in 25 min.
3	Butanol	Red brown	Brown precipitate	Completely decolorized —15 min.
4	Blank	No change	No change	No change

* Suspension of manganese dioxide present most in No. 1.

The more rapid oxidation of ethanol is usually discussed in connection with the test for the presence of methanol in ethanol. As the test is performed[16] the alcohol is oxidized, then added to fuchsine solution that has been decolorized by sulfur dioxide. The presence of formaldehyde is indicated by the appearance of a deep red color within three to five minutes. This is due to the more rapid removal of sulfurous acid by formaldehyde, as compared to acetaldehyde. One drop of 0.01 per cent. formaldehyde added to 2 cc. of fuchsine aldehyde reagent solution gives a pink color within three minutes, while the same amount of acetaldehyde gives no color, even after ten minutes.

Other experiments along these lines easily suggest themselves; for instance, the ease of hydrolysis of esters can be observed by adding the ester in a test-tube with water or solution, and the rate of the change of pH noted.

[15] B. V. TRONOV, *et al.*, "The velocity of oxidation of alcohols by potassium permanganate," *J. Russ. Phys.-Chem. Soc.*, **59**, 1149–56 (1927); *ibid.*, 1157–72 and 1173–97.

[16] ALLEN, "Commercial organic analysis"; 5th edition, Vol. I, p. 90; GEORGIA AND MORALES, *Ind. Eng. Chem.*, **18**, 304 (1926).

THE REACTIVITY OF HYDROCARBONS

Although, except for the olefins, the hydrocarbons do not undergo oxidation very readily, a simple experiment can be used to bring out some of the general relations between the various groups of hydrocarbons. The permanganate solution described above is used. There is immediate reaction with unsaturated hydrocarbons. The difference in rate is of particular interest, since it serves as a different mode of approach to the study of benzene. Cyclohexane reacts faster than *n*-hexane; in turn cyclohexane reacts much slower than cyclohexene and cyclohexadiene.

Benzene, a cyclohexatriene, is expected to be very reactive, and yet it is unaffected by permanganate. The relations between cyclohexane, cyclohexadiene, and cyclohexatriene can be pointed out. The student can see an increased reactivity from cyclohexane to cyclohexadiene with stepwise dehydrogenation, until a cyclohexadiene is converted to benzene, when the unsaturated properties of the system vanish, and a stability similar to saturated compounds is acquired. At the same time the oxidation reaction shows the difference between benzene and naphthalene. The results with the rates of oxidation of various hydrocarbons are given in Table 6.

Experimental.—To five cc. of alkaline permanganate, made as described above, add the hydrocarbon, shake for half a minute, observe any change, then set aside for one-half hour at room temperature. It is important that the hydrocarbons should be of the highest purity.

TABLE 6

RATE OF OXIDATION IN ALKALINE PERMANGANATE OF SOME HYDROCARBONS

(Ten drops of the hydrocarbon added to 10 cc. of 0.03% alkaline permanganate solution)
Concentration of (OH) 0.1 *N*

		Color Changes of Solution		
No.	*Hydrocarbon*	*1 minute*	*30 minutes*	*60 minutes*
1	*n*-Pentane	No change	Slight change	Partial loss of purple color
2	*iso*-Pentane	No change	Slight change	More than 1
3	*n*-Hexane	No change	Slight change	More than 1
4	Cyclohexane	No change	More than 1	Green—more than 2
5	Cyclohexene	Green	Complete—15 min.	
6	Benzene	No change	No change	No change
7	Naphthalene	No change	Same as 1	Same as 1

Similar comparative tests can be made with other reagents. The addition of a bromine solution in carbon

tetrachloride will show the difference in reactivity toward this reagent of the unsaturated hydrocarbons. Another test can be performed with a mixture of nitric and sulfuric acids at 40 to 50°C. to show the difference in the rate of reaction with nitric acid between the benzenoid and non-benzenoid hydrocarbons. In this test, the cyclohexene and cyclohexadiene are omitted, as they react immediately with explosive violence with these acids.

From experience with students over a period of several years, it was found that beginners do well with this type of work.

The compounds which are used in the experiments described, are all available in the market, and inasmuch as 25 g. are more than sufficient for a class of forty, the cost is not prohibitive. It has been found advantageous to place the organic compounds in 25-cc. bottles provided with stoppers having a dropper at the end. The bottles are placed on the dispensing shelf or table, but caution must be used that the students replace the dropper in the proper bottle. The halides should be tested for the presence of free halogen acid by the addition of a drop to 0.5 cc. of long-range indicator. If free halogen acid is present the halide is shaken for a minute or two with a very small amount of solid anhydrous sodium carbonate and filtered through a filter paper. The *n*-pentane, *iso*-pentane, and *n*-hexane used in this work were obtained by careful fractionation of the commercial grade of these hydrocarbons furnished by the Viking Petroleum Company, Charleston, West Virginia. Cyclohexene is easily made from cyclohexanol.

A NEW ORGANIC REAGENT *for* BISMUTH

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QUINOLINE-potassium iodide solution has been investigated as a sensitive reagent for bismuth by Korenman[1] and Gapchenko and Sheĭntzis.[2]

The similarity in reaction properties of the quinolines and the benzothiazoles was pointed out by Hofmann.[3] It was this relationship that led to the present investigation of 2-methyl benzothiazole-potassium iodide solution as a reagent for bismuth. 2-Methyl benzothiazole in alcohol solution with potassium iodide reacts readily with bismuth to give red-orange needles, and with antimony to give yellow needles.

EXPERIMENTAL

Reagent.—2-Methyl benzothiazole was prepared according to the method of Naiman and Bogert.[4]

Test solutions were made according to the directions of Curtman[5] to contain 100 mg. of metal ion per ml. of solution, with the exception of arsenic, aluminum, and magnesium.

Sensitivity of Test for Bismuth.—All dilutions of the 100 mg. per ml. solution of bismuth were made with 3 *M* nitric acid, up to and including 5 mg. per ml. More dilute solutions were made with distilled water. In each test, 1 ml. of 1 *M* potassium iodide was added to the test solution first, followed by 1 ml. of a one per cent. alcoholic solution of 2-methyl benzothiazole.

TABLE 1

5 Ml. of Bi solution mg./ml.	*Immediate Reaction Color*	*Turbidity*	*Crystals*
0.050	red-orange	marked	red needles—15 min.
0.025	red-orange	moderate	red needles 2 hr.
0.020	red-orange	slight	red needles 2 hr.
0.0125	red-orange	faint	red micro-crystals—4 hr.
0.010	negative	negative	red micro-crystals—24 hr.

According to the results summarized in Table 1, it may be seen that the sensitivity is 1 part in 50,000.

Spot Plate Test.—0.001 ml. or 1 cmm. of a solution containing 0.05 mg. bismuth per ml. was placed in the depression of a white porcelain spot plate, mixed with 0.001 ml. or 1 cmm. of 1 *M* KI and 0.001 ml. or 1 cmm. of a one per cent. solution of 2-methyl benzothiazole produced an immediate red turbidity.

Micro Test.—On a slide under a microscope, with reflected light, 0.001 ml. of a solution containing 0.05 mg. bismuth per ml. produced with 0.001 ml. of 1 *M* KI and 0.001 ml. of a one per cent. solution of 2-methyl benzothiazole long red needles, frequently crossed.

Sensitivity of Test for Antimony.—The tests for antimony were carried out in a similar manner to those for bismuth, and it was found that 5 ml. of a solution containing 0.02 mg. antimony per ml. produced with the reagents a yellow turbidity; yellow needles settled in two hours. The sensitiveness of this test for anti-

[1] KORENMAN, *Z. anal. Chem.*, **99**, 402–10 (1934).
[2] GAPCHENKO AND SHEĬNTZIS, *Zavodskaya Lab.*, **4**, 835 (1935) (through *Chem. Abstr.*, **30**, 984 (1935)).
[3] HOFMANN, *Ber.*, **20**, 2264 (1887).
[4] NAIMAN AND BOGERT, *J. Am. Chem. Soc.*, **57**, 1661 (1935).
[5] CURTMAN, "Qualitative chemical analysis," The Macmillan Co., New York City, **1931**, p. 502.

mony is therefore the same as for bismuth, *i. e.*, 1 part in 50,000.

Test for Bismuth in the Presence of Antimony.—The precipitate formed by bismuth and the reagents is deep enough in color to be evident even in the presence of considerable amounts of antimony. One ml. of solution containing 0.5 mg. antimony per ml. was mixed with 1 ml. of a solution containing 0.05 mg. bismuth per ml.; 1 ml. of 1 *M* potassium iodide was then added, followed by 1 ml. of one per cent. 2-methyl benzothiazole; an orange turbidity formed, which changed to red-orange needles in fifteen minutes. Sensitiveness: Bi:Sb = 1:10.

Other Interferences.—The metals of Group I, Ag^{+}, Pb^{++}, and Hg_2^{++} form precipitates on adding potassium iodide, which might interfere with the detection of bismuth. However, if to a solution of these ions and bismuth, 1 *M* potassium iodide is added in sufficient excess to precipitate the Group I ions completely and to form a yellow supernatant solution of BiI_4^{-}, and the precipitate is then filtered off, the filtrate forms the characteristic red-orange precipitate on adding one per cent. solution of 2-methyl benzothiazole.

One ml. of Group I test solution, containing 2 mg. Ag, 1 mg. Hg_2^{++}, and 6 mg. Pb was mixed with 1 ml. of a solution containing 0.5 mg. of bismuth; 1 *M* potassium iodide was added until precipitation was complete and the precipitate readily coagulated. The precipitate was filtered off and 0.5 ml. of one per cent. solution of 2-methyl benzothiazole was added to the filtrate; a heavy red-orange precipitate formed. If 1 ml. of solution containing 5 mg. of bismuth is present in the above Group I test, it may be detected in the supernatant solution without filtering. A control test on 1 ml. Group I test solution was run by adding 1 *M* potassium iodide solution until precipitation was complete and then 0.5 ml. of a one per cent. solution of 2-methyl benzothiazole was added. The whole was allowed to stand. The reagent seemed to cause more rapid coagulation of the iodides, but no change in the color of the precipitate was noted in five hours.

Cu^{++} and Fe^{+++} react with potassium iodide to liberate free iodine which obscures the bismuth test. Sodium bisulfite, however, removes the free iodine and the test for bismuth becomes definite. One ml. of solution containing 20 mg. Cu^{++} was mixed with 1 ml. of solution containing 0.5 mg. Bi^{+++}. One ml. of 1 *M* potassium iodide was added; the brown mixture was treated with three drops of five per cent. solution of sodium bisulfite (or until the brown color just disappeared) leaving the yellow color of bismuth iodide solution and a white precipitate; 1 ml. of one per cent. 2-methyl benzothiazole produced a heavy red-orange precipitate.

In a like manner 0.5 mg. of Bi^{+++} was detected in the presence of 20 mg. of Fe^{+++}.

Hg^{++} does not interfere if sufficient excess of potassium iodide solution is added to dissolve the precipitated mercuric iodide. One ml. of solution containing 0.1 mg. of Hg^{++} forms a white crystalline precipitate with 2-methyl benzothiazole (with or without potassium iodide). This reaction is to be further investigated.

The remaining ions of Group II do not interfere with the test for bismuth. Two ml. of a solution containing 4 mg. each of Hg^{++}, Pb^{++}, Bi^{+++}, Cu^{++}, As^{+++}, Sb^{+++}, As^{+++++}, and Sb^{+++++} and 8 mg. each of Cd^{++} and Sn^{++++} was mixed with 2 ml. of five per cent. solution of sodium bisulfite and 2 ml. of 1 *M* potassium iodide. A yellow turbidity formed. This suspension was divided into two parts. The first part was allowed to stand as a control and a yellow precipitate soon settled out; the second part, when treated with 1 ml. of a one per cent. solution of 2-methyl benzothiazole, yielded a red-orange precipitate which increased in amount on standing. A similar solution containing all of the above ions except Bi^{+++} was treated in the same manner. Only a yellow precipitate formed. AsO_3^{---}, AsO_4^{---}, Sn^{++}, SbO_3^{---}, and SbO_4^{---} do not interfere.

The ions of Group III, other than Fe^{+++}, do not interfere when tested individually or as a whole. One ml. of a solution containing 4 mg. each of Al^{+++}, Cr^{+++}, and Zn^{++} and 2 mg. each of Fe^{+++}, Co^{++}, and Mn^{++} was mixed with 1 ml. of a solution containing 0.5 mg. Bi; 1 ml. of 1 *M* potassium iodide was added. To the brown solution, five per cent. sodium bisulfite was added until the color changed to yellow; then 1 ml. of one per cent. solution of 2-methyl benzothiazole was added. A red-orange turbidity formed, and red needles settled in a few minutes. Fe^{++} does not interfere.

The ions of Groups IV and V do not interfere with this test for bismuth. One ml. of a solution containing 4 mg. each of Ba, Sr, and Na and 2 mg. each of Ca, Mg, K, and NH_4^{+} was mixed with 1 ml. of a solution containing 0.5 mg. Bi and only 1 mg. KI. A clear yellow solution resulted; when 1 ml. of a one per cent. solution of 2-methyl benzothiazole was added an orange-red turbidity formed, from which red needles settled out in one hour. A control solution of Groups IV and V treated with 1 ml. of 1 *M* potassium iodide and 1 ml. of one per cent. 2-methyl benzothiazole remained clear and colorless after standing four hours.

Large amounts of iodide, cyanide, bisulfite, and thiosulfate dissolve the bismuth precipitate and inhibit the test. The test is also inhibited by nitric and hydrochloric acids more concentrated than 3 *M* and by concentrated NH_4OH.

Analyses.—A sample of the purified crystalline precipitate was analyzed for iodine by titrating a weighed sample with standard potassium iodate according to the method of Andrews.[6]

Calculated for $C_8H_7NS{\cdot}KBiI_4$: I, 56.11. Found: Iodine, 56.04. Another sample of the precipitate was evaporated twice with concentrated nitric acid and then with sulfuric acid and ignited carefully to form K_2SO_4 and $Bi_2(SO_4)_3$.

Calculated for $C_8H_7NS{\cdot}KBiI_4$: $K_2SO_4 + Bi_2(SO_4)_3$, 48.62. Found: $K_2SO_4 + Bi_2(SO_4)_3$, 48.46.

[6] ANDREWS, *J. Am. Chem. Soc.*, **25**, 756 (1903).

These analyses correspond to the formula $C_7H_4S(N)$-$CH_3 \cdot KBiI_4$.

SUMMARY

A mixture of a one per cent. solution of 2-methyl benzothiazole in 95 per cent. alcohol and 1 *M* potassium iodide is a sensitive reagent for bismuth and antimony.

Bismuth may be detected in the presence of antimony and all the other cations encountered in the usual qualitative analysis scheme by the deep red-orange color of the bismuth precipitate.

Copper and ferric ions interfere, due to the formation of free iodine, but the interference is eliminated by sodium bisulfite.

Mercuric ion forms a white precipitate with 2-methyl benzothiazole alone.

A DISPLAY WINDOW LABORATORY

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SINCE many junior colleges and other institutions of learning are supported from public funds, we believe that methods of advertising, such as described here, create a more friendly attitude toward the schools in the mind of the average citizen. We feel that this account of our window displays may offer suggestions to others who may be interested in similar projects.

Saturday, November 2nd, was our Junior College Day at a big local department store. Seventy-five students were employed by the store as extra clerks, but probably the most interesting part of the event was the window displays which were witnessed by tens of thousands of people.

The physics exhibit consisted of a photoelectric cell placed in a beam of light which could be intercepted by a spectator outside of the window. This action caused lights within the window to be turned on and an electric motor to start.

In the aeronautics department window, several students were constructing the wing of a plane, while in another window students from the art department were drawing portraits. The geology department exhibit consisted of a beautiful collection of minerals and a student performing tests.

Since the organic chemistry exhibit was probably the most spectacular and received so much favorable comment, we will describe it in more detail.

The window space was about twenty feet long by seven feet wide. In the center was placed a table with test-tubes, beakers, a balance, a microscope, and chemicals for the synthesis of paranitroaniline red, osazones of sugars, and recrystallizations of dinitrobenzene and acetanilide. On the wall behind the table was a periodic chart, a large benzene ring in jet black on a white background, a blackboard, and a large college banner. On one side in front of the table were six sets of apparatus for steam distillation, a Grignard synthesis using stirring motor, bromobenzene synthesis, and three sets of apparatus for fractional distillation. One of these was equipped with a Vigreux column, 170 cm. long, constructed from the top of a broken distilling flask and a Pyrex glass tube, 3 cm. wide. The other two were equipped with Hempel columns, 3.5 cm. wide. and nearly two meters long. These were filled with clean, white quartz pebbles instead of the traditional glass beads. Each set of apparatus was attached to a single large ring stand (condensers vertical) and the six sets clamped together to give greater stability. Methanol lamps were used for heating. These cost almost nothing when each is made from a discarded stock bottle, a cork, piece of glass tubing which must not reach below the level of the methanol, a wick made from ordinary cotton twine and a flat, circular, tinned iron plate placed on top of the cork. The greatest care was exercised to avoid chemicals with odors and danger from fire. Only water was placed in the six sets of apparatus. On the other side of the table was placed a series of specimen bottles and a chart showing products obtained in the synthesis of paranitroaniline red from coal. Behind these was a row of about forty books dealing with different fields of organic chemistry. Two twelve-liter balloon flasks, each protected by being set in a large mixing bowl, served as book ends. Each contained a fermenting mixture of sugar solution and yeast and was equipped with a glass tube which led the evolved carbon dioxide so that it would bubble through water. About thirty copies of periodicals, *Chemical Abstracts*, *Industrial and Engineering Chemistry*, *Journal of the American Chemical Society*, JOURNAL OF CHEMICAL EDUCATION, *Chemical & Metallurgical Engineering*, *Chemical Industries*, etc., were arranged near the window glass in front of the whole exhibit. Many of these were open to show typical articles. A number of charts, diagrams, signs, etc., explained the operation of the different sets of apparatus.

To increase the artistic appeal of the exhibit, all ring stands, test-tube racks, large tin cans for water baths, waste, etc., were painted a brilliant Chinese red. These were placed on a background of white oilcloth. Several students, each dressed in a white laboratory coat, worked in this display window laboratory. Some gave demonstrations of dyeing with paranitroaniline red, while others practiced writing equations on the blackboard or otherwise conducted themselves in a scholarly manner.

On the whole we consider our window display not only a public scientific demonstration but a work of art and a creation of beauty.

The NITROGEN AFTER-GLOW

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I. INTRODUCTION

THE study of the phenomena resulting from the passage of electric currents through rarified gases has provided much information of interest to chemists. One of the best understood of such topics, from the physical-chemical standpoint, is that concerned with nitrogen in the activated state. This subject attracted attention early because of the beauty of many of the electric displays obtained, and because the subject is relatively simple and not difficult to study.

In 1891 J. J. Thomson (*1*) passed a high-frequency alternating current through a coil of a few turns of heavy wire surrounding a glass vessel which contained gas at low pressure. He found that a luminous discharge in the form of a ring was produced in the gas. This type of gaseous conduction is now known as the "electrodeless" discharge.

In 1899 E. P. Lewis (*2*) passed a condenser discharge through nitrogen gas at low pressure, and was rewarded with the observation of a new phenomenon, which he called "nitrogen after-glow." He found that under certain conditions the usual discharge gave place to an intense yellow glow pervading the entire volume of the vessel and persisting for a considerable time after the discharge itself was discontinued.

It remained, however, for R. J. Strutt (later Lord Rayleigh) (*3*) to undertake in 1911 a systematic study of the phenomenon. He and subsequent investigators have made exhaustive observations on different phases of the problem, and plausible theoretical discussions have been published to account for the observed facts.

II. EXPERIMENTAL OBSERVATIONS

For the establishment of the optimum nitrogen after-glow the following external, or environmental, conditions must be satisfied and adjusted more or less carefully: (*a*) the chemical content of the gas, (*b*) its pressure, (*c*) the electric discharge circuit, and (*d*) the time during which the discharge is allowed to pass.

It has been found by a number of authors that absolutely pure nitrogen will not give an after-glow; slight traces of electronegative gases are necessary. Bonhoeffer and Kaminsky (*4*) in 1926 reported that the maximum effect of H_2S lies at 0.04 per cent.; of CH_4 at 0.1 per cent.; of O_2 at 0.23 per cent.; and that less than 0.03 per cent. of O_2 has no effect. They state further that at more than 0.5 per cent. O_2 the glow is extinguished. On the other hand, Pirani and Lax (*5*) earlier found that in a glass vessel of two liters capacity under a discharge of about 100,000 cycles per second, the maximum effect was obtained when the impurity was present to an extent of only about 0.0015 per cent., the effect being reduced when the concentration was raised to 0.006 per cent.

Nevertheless, authorities agree that absolutely "glowless" nitrogen can only be produced by baking out the discharge vessel and taking precautions (as by the insertion of liquid-air traps) against mercury vapor, stopcock grease, and other impurities from the vacuum system. It appears (*6*) that for the after-glow to appear the glass surface in contact with the nitrogen must be contaminated with a layer of molecules of O_2, H_2O, H_2S, etc. Solid paraffin serves effectively to contaminate the surface; glowless nitrogen cannot be produced in paraffin-lined containers.

That oxygen (or other impurity) is necessary to the actual *production* of the activated nitrogen, not merely for the existence of the after-glow, is shown by the fact (*7*) that when oxygen is introduced into a vessel containing pure, glowless nitrogen immediately after discontinuation of the discharge, no glow is induced.

The pressure of the nitrogen is not critical. The maximum duration of glow occurs (*6*) when the pressure is about 0.04 mm. of mercury. However, it will occur at any pressure which will permit passage of the electric discharge, namely, up to several millimeters.

An intense after-glow has been obtained (*8*) in a mixture of 0.2 per cent. nitrogen and 99.8 per cent. argon at 300 mm. In this mixture, the partial pressure of nitrogen is 0.6 mm., which is well within the limits of pressure requisite for the usual glow in pure nitrogen. Thus, it may be concluded that the partial pressure of nitrogen only is important, the total pressure due to inert gases having little or no effect.

The after-glow may be excited by the electrodeless ring discharge described above, or by the condensed electric discharge between electrodes. In the latter case the terminals are usually made of aluminum, platinum, or tungsten; copper cannot be used (*9*) as it has a strong catalytic action, accelerating the decay of the glow to such an extent that it may not be observable at all. A spark gap must be inserted in parallel with the discharge tube.

It should be mentioned that nitrogen in the proximity of radioactive substances presents the chemical activity characteristic of active nitrogen (*10*).

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It is found (*11*) that the duration of the after-glow apparently falls off exponentially with increased time of discharge.

The period of discharge may determine not only the duration but also the appearance of the discharge. Lewis reports (*12*) that "different types of after-glow may be excited in the same mixture of nitrogen and oxygen at the same pressure merely by altering the time of discharge. At 0.53 mm. pressure in air, a one-half second discharge gives rise to a blue after-glow, while an instantaneous discharge leaves a yellowish-green after-glow." (Glows of color other than yellow sometimes occur in nitrogen-oxygen mixtures due to the fact that oxygen becomes activated as well as nitrogen.)

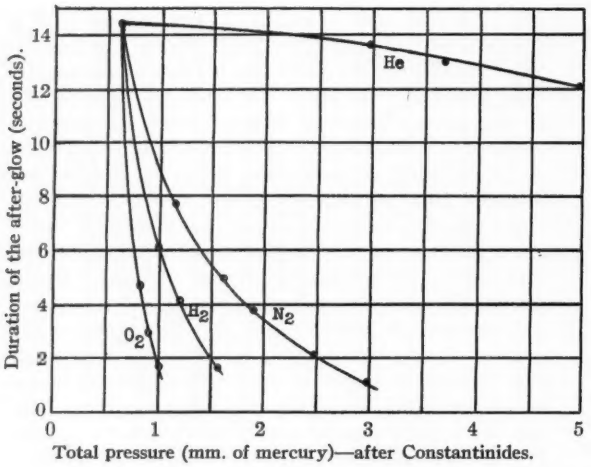


FIGURE 1

An entirely different effect due to the time element has been noted. If a quantity of nitrogen be sealed into a discharge vessel and its after-glow excited periodically over an extended period of time, the duration of the glow is found to vary with the time of storage. Knipp (*13*) gives the following data for nitrogen at an appropriate pressure in a twenty-two-liter Pyrex flask, duration of each discharge, 0.1 second.

Date	*Interval*	*Duration*
April 10, 1930	0 days	35 minutes
August 12, 1930	122 days	110 minutes
March 4, 1931	324 days	187 minutes
October 18, 1931	553 days	165 minutes

"Apparently the duration of the after-glow reached a maximum in about a year." No theoretical explanation of this has been offered.

The considerations above have reference to the initial establishment of the glow. Of interest also are the effects of treating the gas in certain ways while the glow is taking place.

The chief phenomena other than chemical which have been observed in glowing nitrogen are the effects of heat, cold, electric discharge, and pressure.

If the apparatus be arranged so that nitrogen is drawn through a long glass tube, the glow may easily be observed all along the length of the tube. If this be heated locally, the glow is destroyed or "quenched" beyond the heated portion.* The glow is similarly quenched by a small electric discharge through the gas. If the glowing gas is passed through a liquid air trap, the glow is greatly intensified within the trap, and its duration is diminished. The glow is greatly increased by compression, but when the former volume is restored the capacity to produce the glow is exhausted. It is not affected by electric or magnetic fields (*14, 15*).

Some of the most interesting phenomena concerned with nitrogen in the excited state are those occurring when the gas comes in contact with various foreign substances, both gases and solids.

The effects on the duration of the after-glow of certain gases admitted immediately after cessation of the discharge are shown in Figure 1. In the case of oxygen, considerable energy is taken up by the O_2 molecules from the active nitrogen, thus decreasing the life of the latter. Apparently energy is not transferred as readily to hydrogen or to unactivated nitrogen. Practically no energy is given to helium molecules, either as increment to their internal energy or to their translational energy.

Similar results are shown in Figure 2 for gases admitted before activation takes place. The principal difference here is in the case of oxygen, which itself becomes activated by the discharge, causing a maximum to appear in the curve, accompanied by a glow of a brilliant green color. The nitrogen curve in Figure 3 merely serves as a standard with which to compare the others; it shows only the effect of increased pressure (*10*).

Ordinary gaseous nitrogen, as is well known, will not react with hydrogen under ordinary conditions. However, activated nitrogen will combine with activated hydrogen to form ammonia and hydrazine. For this reaction to occur it is necessary that both gases be activated; neither alone is sufficient (*16*).

When iodine vapor is exposed to active nitrogen with a comparable pressure, "the visible reaction is an instantaneous flash. Cinema studies indicate that even with imperfect mixing, the duration of the reaction is less than one one-hundredth of a second. It is extremely unlikely, however, that there is any chemical action; the iodine merely receives energy and radiates it again" (*17*).

"The luminosity of the halogens is in this manner excited with increasing intensity in the order chlorine, bromine, iodine. Hydrogen is caused to react with

* According to Willey (*J. Chem. Soc.*, **1927**, 2831) the glow is enhanced by heating to 225°C., destroyed by heating to 300°C., and then only exceptionally reappears on cooling (*14*).

chlorine, but not bromine or iodine. Conversely, HBr and HI, but not HCl are decomposed." (*18*).

The action with hydrobromic acid has been studied in detail by Ewart and Rodebush, of the University of Illinois (*19*). I quote the original paper at length, as it gives a graphic acount of a typically spectacular phenomenon in this field.

"HBr at low pressure was introduced into a tube through which glowing nitrogen, also at low pressure, was flowing. The point of introduction of the HBr was about 30 cm. from the discharge bulb. . . At the point where the HBr was admitted the after-glow became a brilliant orange of greatly increased intensity and all after-glow ceased in the tube beyond the point of admission. After a few minutes a white deposit appeared on the walls of the tube at the point of admission of the HBr. The solid proved to be NH_4Br, and at the end of the run the liquid air trap (near the vacuum pump) was found to contain free bromine.

"When the HBr flow was stopped the brilliant orange flame diminished in intensity and moved at the rate of a few centimeters per minute toward the pump. By the time the flame had moved some 20 cm. its intensity was apparently reduced to zero, and the normal yellow after-glow suddenly swept through the apparatus as though a valve had been opened. When the flame was allowed to 'die out' in this way no white deposit remained in the tube. In order to obtain samples of the white deposit it was necessary to stop the flow of active nitrogen at the same time as the HBr.

"When HI is introduced in place of HBr, the same phenomena were observed and the flame was even more intense and of a brilliant blue color. With HCl, no effect was observed except that the after-glow ceased below the point of admission."

The reactions suggested by the authors to account for these phenomena are as follows.

$$N + HI \longrightarrow NH + I - 35 \text{ cal}$$
$$N + HBr \longrightarrow NH + Br - 15 \text{ cal}$$
$$N + HCl \longrightarrow NH + Cl + 5 \text{ cal (does not take place)}$$

In the particular case of hydrogen bromide, the mechanism is thought to be as follows.

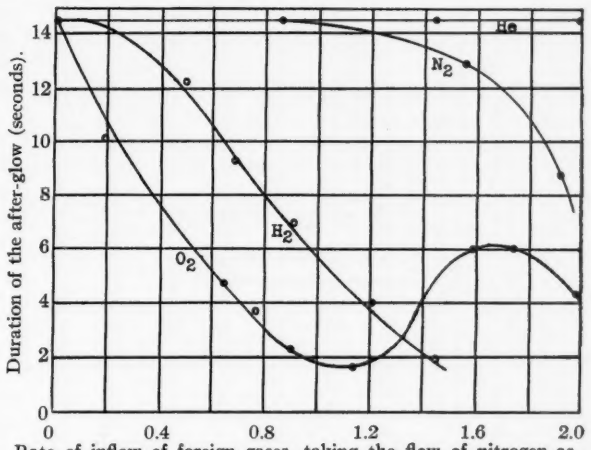
$$N + HBr \longrightarrow NH + Br$$
$$NH + HBr \longrightarrow NH_2 + Br$$
$$NH_2 + HBr \longrightarrow NH_3 + Br$$
$$NH_3 + HBr \longrightarrow NH_4Br$$

"Complete cessation of after-glow below the point of admission must be attributed to the catalytic action of the NH_4Br on the walls of the tube in deactivating the nitrogen, since this effect persists after the flow of HBr is stopped. This deactivation, however, liberates heat and the NH_4Br sublimes molecule by molecule and travels slowly down the tube. When the NH_4Br sublimes, however, it dissociates into HBr and NH_3, and the above reactions occur again. The NH_4Br is thus all used up and the Br_2 is eventually all collected in the liquid air trap. . . ."

Active nitrogen interacts also with certain metals, and not with others. The quenching effect of many metals, notably copper, has been mentioned above. Mercury apparently has no effect (*10*). Kenty and Turner of Princeton have reported (*20*) an action of interest on tungsten. "A fine tungsten filament at 400° in active nitrogen is quickly covered with a layer which produces a lowering of resistance of the filament. This lowering of resistance is apparently the result of a lowering of the temperature of the filament because heat is more readily conducted away from the coated filament by the gas than from the clean filament. At a given temperature fifteen to twenty per cent. more heat is conducted away. Traces of oxygen cause the spontaneous formation of a layer which renders the filament insensitive to active nitrogen. Traces of hydrogen prevent the formation of the nitrogen layer and remove it if already present. The amount adsorbed is of the order of magnitude of the quantity required for a layer of single atoms."

Many inorganic salts are caused to phosphoresce by contact with active nitrogen (*21*), while others show no effect (Table 1). In a number of cases the glow lasts several seconds. The color is bluish green. It seems possible that the phenomenon is due to chemical reactions with the active nitrogen or possibly to the presence of free electrons, but as to why certain salts show the action while others, in many cases containing the same anions or cations, do not, nothing is known.

Up to this point the terms "glowing nitrogen" and "active nitrogen" have been used interchangeably. However, E. J. B. Willey (*22*) has shown that glowing, chemically active nitrogen "may be made to lose its luminosity without appreciably affecting its activity, by passing it through a weak electric discharge. Too strong a discharge, however, destroys both effects. The two forms, it appears, are quite distinct, although coexistant. . . . No simple relation exists between the intensity of glow and the amount of active nitrogen present."



Rate of inflow of foreign gases, taking the flow of nitrogen as unity—after Constantinides.

FIGURE 2

One other phenomenon, of a physical rather than chemical nature, should be noted, and that is the extraordinary electrical conductivity exhibited by glowing nitrogen. It is generally conceded that glowing active nitrogen does not essentially contain ions or charged particles of any sort, though these are often present as a subsidiary result of the electric discharge. Kichlu (*23*) and Constantinides (*10*) independently measured the conductivity of the active nitrogen after all ions had been removed by suitable electrodes. Kichlu found that nitrogen so treated showed no trace of conductivity, while Constantinides obtained com-

paratively large values even after carefully removing all ions. He ascribes the conductivity to electrons ejected from the cathode by a photoelectric effect produced by the glow of the nitrogen. This conflict of

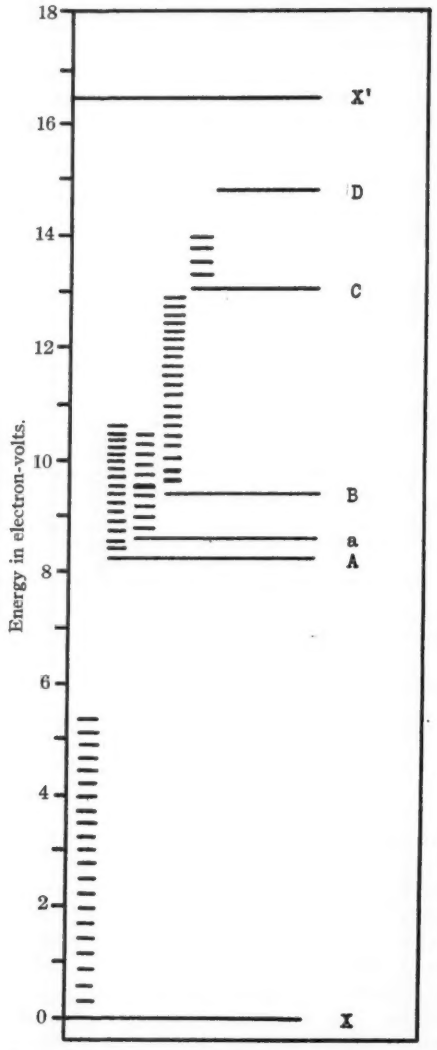


FIGURE 3.—ENERGY LEVELS OF N_2 MOLECULE (FROM KNAUSS)

results has not yet been definitely settled. It seems certain, however, that at least under some conditions active nitrogen will carry a current independently of ions coming from the discharge tube.

III. THEORETICAL DEDUCTIONS

Information as to the energy relations connected with activated nitrogen may be obtained by two methods, spectrum analysis and direct experimental determinations.

By the latter method, for example, it has been found (*10*) that no effect is produced when mercury vapor is introduced into active nitrogen, while iodine gives a color effect and a marked increase in the number of ions

TABLE 1

EFFECT OF ACTIVATED NITROGEN ON CERTAIN SALTS

Phosphorescent		*Non-phosphorescent*	
$UO_2(NO_3)_2$	$AlCl_3$	CaS	KNO_3
Na_2CO_3	LiCl	$CaCO_3$	HgBr
ZnS	NaCl	K_2SO_4	
$CaCl_2$	KCl	KOH	etc.
$SrCl_2$	CsCl		
$BaCl_2$	KI		

present. As the ionization potentials of mercury and iodine vapors are known by direct measurement, it is evident that active nitrogen must contain a species of particle with energy between 9.0 (I_2) and 10.4 (Hg) electron-volts. Furthermore this species must be metastable, as its rate of decay is rather slow.

The accompanying chart (Figure 3) after H. P. Knauss (*24*), shows the various possible energy levels and sublevels of the nitrogen molecule. In this diagram the level *X* represents the normal, or unexcited condition of the molecule. *A*, *a*, *B*, *C*, and *D* are electronic states of successively higher energy content, while the numerous sub-levels represent the various vibrational states possible within each electronic state. In the spectra of electric discharges of various sorts in nitrogen, lines corresponding to many of the various possible energy transitions may be observed, and the reactions taking place in the discharge largely determined. The chief bands characteristic of the afterglow represent transitions from the 10th, 11th, and 12th sub-levels of state *B* to the 5th, 6th, 7th, and 8th state *A* (*24*). By these means the mechanisms of the reactions and energy transformations taking place in active nitrogen have been fairly conclusively determined. I quote Rodebush (*25*).

"The after-glow [of activated nitrogen] is due to the emission of radiation by a molecule or atom in an excited state, but the difficulty lies in accounting for its persistence.

"The immediate result of the discharge is to produce ions that are neutralized as soon as the discharge ceases. Under favorable conditions these atoms do not combine on the walls of the tube, but only in a triple collision with another nitrogen molecule. As a result of this collision two nitrogen molecules are produced, one of which is in an excited state

$$N + N + N_2 \longrightarrow N_{2A} + N_2$$

The fact that a triple collision is required means that this reaction will itself be slow. The molecule N_{2A} is now in a metastable state; it cannot lose energy by radiation. The only way in which the molecule N_{2A} can lose its energy is by collision with another molecule likewise in the A state

$$N_{2A} + N_{2A} \longrightarrow N_2 + N' + N'$$

These collisions will not occur very frequently, since the concentration of N_{2A} is small. As a result of this collision one normal and two excited atoms (N′) are produced. These excited atoms are likewise in a metastable state. They can lose their energy only by collision with an activated molecule

$$N' + N_{2A} \longrightarrow N_2 + N + h\nu$$

As a result of this collision the radiation of the after-glow is produced. It is not of a single frequency, because the rotational and vibrational energy of the N_{2A} molecule is a variable quantity and also because there are apparently two metastable states differing by 1.2 volts possible for the atom N′. A nitrogen atom in the normal state is produced by this reaction. This atom will now go through the cycle again. In view of the fact that all of the mechanisms shown above involve collisions that are relatively infrequent, it is not surprising that active nitrogen has a long life.

"One other interesting fact needs to be explained. If a weak discharge is passed through active nitrogen, or if the active nitrogen is heated, the after-glow ceases. The explanation of this cessation is that a small amount of energy serves to raise the N_{2A} molecule to the energy level *a* of Figure 3 (from the level *A* previously occupied). This level is not metastable and its energy can be lost immediately by radiation. In this process the nitrogen molecule returns to its normal state."

The independence of the glow and chemical activity is thus explained (*22*). The activated nitrogen consists of a mixture of metastable diatomic molecules (N_{2A}) responsible for its chemical activity, and a much smaller proportion of atoms (N′) which on recombination release their energy (at least in part) as luminescent radiation. The proportional numbers of these different species is not necessarily constant and may be altered by physical means, thus accounting for certain of the observations previously mentioned.

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THE SIXTEENTH EXPOSITION OF CHEMICAL INDUSTRIES

The Sixteenth Exposition of Chemical Industries will present a brilliant pageant of American industrial recovery in terms of the contributions of chemistry and chemical engineering. The Exposition will be held at Grand Central Palace, New York, December 6 to 11, 1937. Three floors of Grand Central Palace have been reserved, and the advance leasing of exhibit space indicates that the 1937 Exposition will be one of the most representative and comprehensive in recent years. Dr. M. C. Whitaker, Vice-President of the American Cyanamid Company and a distinguished figure in the chemical industry, will be Chairman of the Advisory Committee of the Sixteenth Exposition.

Members of the Advisory Committee have just been announced as follows: M. C. Whitaker, Chairman, Vice-President, American Cyanamid Company; Raymond F. Bacon, Consulting Chemist; L. H. Baekeland, Honorary Professor Chemical Engineering, Columbia University; William Callan, President, The Chemists' Club; J. V. N. Dorr, President, The Dorr Company; Henry B. Faber, Consulting Chemist; William G. Harvey, President, The Electrochemical Society; William Haynes, President, *Chemical Industries;* Charles H. Herty, Industrial Consultant; H. E. Howe, Editor, *Industrial and Engineering Chemistry;* Martin H. Ittner, President, American Institute of Chemical Engineers; Sidney D. Kirkpatrick, Editor, *Chemical and Metallurgical Engineering;* Charles Lichtenberg, President, Salesmen's Association of American Chemical Industry; W. T. Read, Dean of Chemistry, Rutgers University; Charles F. Roth, Manager Exposition; H. J. Schnell, General Manager, *Oil, Paint & Drug Reporter;* R. Gordon Walker, Vice-President, Oliver United Filters, Inc.; E. R. Weidlein, President, American Chemical Society.

The Sixteenth Exposition of Chemical Industries will be under the personal direction of Charles F. Roth, who has been similarly responsible for previous expositions. Executive offices are at Grand Central Palace, New York.

A HOME-MADE ELECTRIC FURNACE*

EDWARD BERTOLET AND JOSEPH I. OSER

Simon Gratz High School, Philadelphia, Pennsylvania

THIS article describes a home-made arc furnace designed and built mainly through the efforts of two high-school boys—Edward Bertolet and Harold Miller. The furnace develops a fairly high temperature. Its total cost is less than eight dollars for materials.

Many simple arc furnaces have been described in popular scientific literature. In these, the arc is provided by carbon rods which pass into an insulated chamber. In its simplest form this chamber consists of a flower-pot, lined with a coating of shredded asbestos and containing two holes for the passage of the carbons. Resistance is provided by a "heating element" of the type commonly used in radiant electric heaters.

In the first furnace of this type which we made, these unsatisfactory features were found.

1. It was difficult to keep the arc burning and to regulate it, because the carbons were not well supported.
2. The furnace did not become hot enough to melt even brass, because it did not draw enough current.
3. The furnace was not well insulated.

CARBON-FEEDING DEVICE

To feed the carbons for the arc, the following device was made. The carbons (*A*, Figure 1) are held by screws (*B*) in upright tapped steel blocks (*C*). These are two inches high and $^3/_4$ inch square with a tongue (*D*) on the bottom. This tongue fits into a $^1/_8$-inch groove or slot (*E*, Figure 2) in a support (*F*) for the feeding device. This support consists of a piece of steel nine and three-quarter inches long, one inch wide, and three-sixteenths of an inch thick. It is bent at right angles one and three-quarters inches from each end. Four holes (*G*) are drilled and counter-sunk in the support so that it may be screwed to the wooden blocks (*H*) upon which it rests.

The feeding device consists of a threaded $^5/_{16}$-inch steel rod (*I*) with a handle (*J*) inserted near the end. Turning the handle moves the block and the carbon toward or away from the center of the furnace.

This arrangement was devised by one of the boys mentioned, who made it in the school machine shop. We later learned that "Moissan's work was carried out in a furnace consisting of two horizontal electrodes, mounted so that the distance between the two ends could be adjusted longitudinally by a screw thread."† Moissan's crucible was placed under the arc. Ours was placed above the arc so that it could be more easily removed from the furnace.

ELECTRICAL CIRCUIT

To increase the current drawn by the furnace, and therefore the intensity of the arc, the original 9-mm. carbons were replaced by 14-mm. carbons (*A*). The original single heating element used as a resistor was

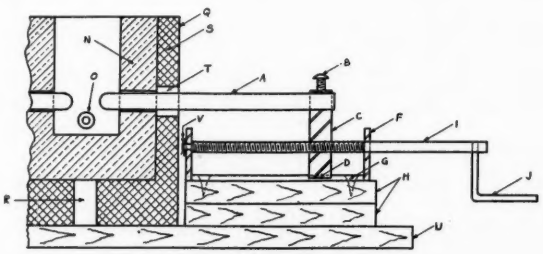

FIGURE 1

replaced by five elements (*K*), connected in parallel (Figure 2). About two feet of wire is removed from each resistor. This enables the circuit to draw a heavier current. A 25-ampere fuse (*L*) is used.

The knife-switch (*M*) shown in Figure 2 is wired so that only two resistors are in circuit when it is open. Closing the knife-switch throws all five resistors into the circuit. The use of two resistors, at first, reduces the starting load. The position of the knife-switch is changed in the drawing, for greater convenience.

INSULATION

The inner core (*N*) is made of fire clay. It is cast in a mold made of a piece of stove pipe four and one-half inches in diameter and six inches long. Two half-inch holes, diametrically opposite each other, are cut into it with a cold chisel midway between top and bottom. These holes allow the passage of the arc carbons.

Next a two-inch cardboard mailing tube, five inches long, is taken. Two half-inch holes, diametrically opposite each other, are cut into it. Their centers are one and one-half inches from the bottom. The bottom of the tube is closed by gluing it with a two-inch circle of cardboard. The exterior is coated with paraffin.

* The furnace which is described here was awarded First Prize in Machine Construction in the Ledger Youth Activities Arts and Handicraft Exhibition in 1937. The contest is sponsored by the Philadelphia Evening Public Ledger.

† PENDER, H., "Handbook for electrical engineers," 1st ed., John Wiley and Sons, Inc., New York City, 1914, p. 565.

A half-inch wooden dowel, six inches long, is inserted through the holes in the mailing tube and stove pipe. This permits the tube to stand upright in the pipe, a short distance above the top. The whole is placed upon a flat board.

The insulation is prepared by adding to three pounds of fire clay enough water to give the mixture the consistency of putty. This mixture is poured into the pipe around the cardboard with frequent tamping. Drying for one week in a warm place is required before the material can support itself. The dowel and paraffined tube can then be withdrawn. The drying causes a shrinkage of about one-half inch in length.

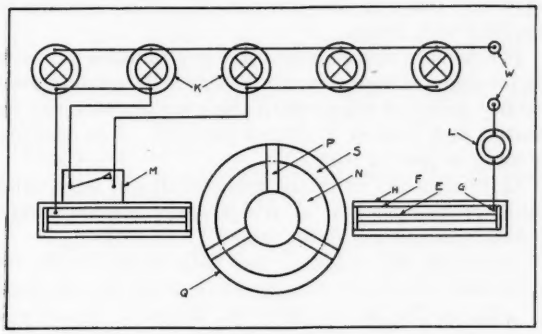

FIGURE 2

Two $^3/_4$-inch holes, to carry the carbons (*O*) for the air holes, are then drilled through the soft material. These are midway between the other two holes, but five-eighths of an inch lower. The carbons (*O*) for the air holes are three-quarters of an inch in diameter and two and three-eighths inches long. The soft core is easily drilled out with a hand drill. Three equidistant grooves (*P*), three-eighths of an inch wide and half an inch deep, are cut into the top of the core. In these grooves rest the chrome steel triangle which supports the crucible.

The core is then placed in the oven of a gas range and gradually heated to 550°F. The temperature can be raised about 100°F. every half hour. The final baking at 550°F. lasts for two hours. The heat is then turned off and the core allowed to remain in the closed oven until it is cold.

A large tomato-juice can (*Q*), seven inches high and six and a quarter inches in diameter, serves as exterior of the furnace. Two one-inch holes for the arc carbons, four and one-eighth inches from the bottom, and the two half-inch air holes, three and one-half inches from the bottom, are made in it with a chisel.

A one and one-half inch length of dry cell carbon (*R*) is then placed upright in the bottom of the can, at the center. This furnishes a firm support for the core (*N*). It is surrounded by tamped shredded asbestos (*S*). The core is then rested on the carbon (*R*) and the holes in the can and core are lined up by inserting the four pieces of carbon required.

Two of these are the arc carbons (*A*), wrapped with a sheet of asbestos (*T*) one and one-half inches wide to just permit their insertion into the one-inch holes. The other two carbons (*O*) are then inserted.

The rest of the space in the can is now filled with shredded asbestos, well tamped. The three grooves (*P*) in the core for the triangle are continued to the edge of the can.

THE LID

The lid is made from a mixture of two-thirds shredded asbestos and one-third fire clay with enough water to permit easy handling. This is placed in a dish (such as an old-fashioned soup plate) about five and one-half inches in diameter and two and one-half inches deep, which contains the wire for the handle.

The handle is made by bending a foot of soft iron wire into a semicircle with three or four inches projecting above as a loop. Another piece of wire, five or six inches long, is bent into a semicircle and hooked on to the larger piece. The part which is to project is then bent over so as to lie flat in the dish.

This is allowed to set for several days. When sufficiently hard a half-round chisel is used to cut out a circle half an inch deep, two and a quarter inches in diameter, on the bottom of the lid. This allows room for the lid of the crucible.

The lid is then baked with the core.

ASSEMBLY

The furnace is mounted on a three-quarter-inch board (*U*) $22^1/_4$ by $13^1/_4$ inches. This is covered with a sheet of asbestos, tacked at the corners. The insulated chamber (*Q*) is fastened to the board by screws through two small brackets. The brackets are simply sheet brass, one inch long and half an inch wide, bent at right angles.

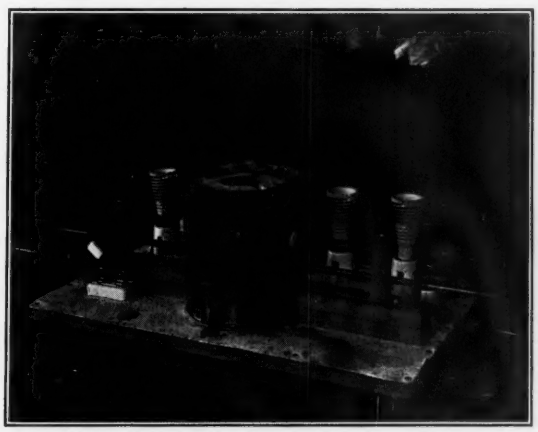

FIGURE 3

The wood blocks (*H*), upon which rest the supports

(*F*) for the carbon feed, are screwed to each other. They are then screwed to the board from the bottom. The supports (*F*) are held to the blocks by four small screws (*G*). Figure 2 shows the furnace at this stage.

Each threaded rod (*I*) is inserted through the upright blocks (*C*) and placed in its support (*F*). Here it is held by a washer and cotter pin (*V*).

The two binding posts (*W*), five resistors (*K*), a knife switch (*M*), and a 25-ampere fuse (*L*) are then fastened to the board and wired up as shown in Figure 2. A wire is fastened to each support (*F*) to make it part of the circuit. This is done at one of the four screws (*G*) which fasten it to the block (*H*).

OPERATION

The furnace will operate equally well on alternating or direct current. Black glasses are absolutely necessary to protect the eyes of the operator when adjusting the arc. Otherwise serious injury to the eyes will occur.

The furnace is started with the knife switch open. As we have explained, only two resistors are then in the circuit. The feeding device is used to touch the carbons to each other and then to withdraw them slightly, producing an arc. At this time a maximum current of about fifteen amperes is drawn which drops as the carbons are separated. The knife switch is then closed. This puts all five resistors into the circuit and the current rises to 25–30 amperes. As the separation of the carbons is continued to make a gap of about one inch, the current drops to slightly over twenty amperes. This produces a good "husky" arc which can be kept in operation for hours by slight adjustment of the feeding device as the carbons are consumed.

The furnace as described will hold a #0 graphite crucible. This is filed slightly on the three points which make contact with the triangle so that the crucible drops to about three-eighths of an inch above the carbons. The flat faces filed on the crucible permit it to fit tightly into the triangle. The latter is made of chrome steel and rests in the grooves (*P*). The crucible is handled with tongs.

The furnace takes about forty-five minutes to reach its maximum temperature. At this stage one hundred twenty grams of clippings of thick copper wire can be melted and poured in fifteen minutes. The melting point of copper is 1083°C.

Molten metals from the crucible should be poured into *dry* receptacles. A dangerous explosion might result from the use of wet sand.

A crucible full of small steel nails seemed to be on the point of fusion as was proven by slight loss of shape of some of the nails. However, the metal would not become fluid. Likewise no success was met in attempting to melt sand.

It is well to have adequate ventilation to guard against emission of carbon monoxide from the furnace. We were not bothered by the gas, but it is best to be wary.

SUMMARY

The construction of a small arc furnace, costing about eight dollars for materials, is described in detail. It is believed that teachers of chemistry will find this a splendid project for groups of boys who are mechanically adept.

A SIMPLE METHOD OF MAKING QUINONE

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THE approved method of making benzoquinone in the laboratory[1] seems to be that of oxidizing hydroquinone with bichromate and sulfuric acid, followed by filtration, extraction with benzene, and distillation with steam. The process involves three or four operations, which require several hours and the yield leaves something to be desired.

The procedure here described which can be carried out in 30 minutes, gives a practically quantitative yield of quinone of exceptional purity. The reaction is the following: $3C_6H_4(OH)_2+KBrO_3 \rightarrow 3C_6H_4O_2+KBr+3H_2O$.

A little sulfuric acid, an active catalyst for the reaction, is required.

A mixture of 10 g. of hydroquinone, 5.5 g. of potassium bromate, 100 ml. of water, and 5 ml. of normal sulfuric acid is warmed to 60° in a 200-ml. flask. The solids dissolve and the reaction starts promptly, giving first nearly black crystalline quinhydrone as an intermediate product. Without further heating, the temperature rises spontaneously to about 75°. After ten to fifteen minutes the oxidation is complete, the dark color changing to the clear bright yellow of quinone. The mixture is then heated to 80° to dissolve the quinone completely, cooled to zero, filtered and washed free of potassium bromide with a little ice water, and dried. No by-products are formed. The quinone is crystalline and exceptionally pure.

The proportion of sulfuric acid seems to be critical. With no added acid the reaction is slow and incomplete; with 12 ml. of normal acid added to the solution at 60°, the temperature rises rapidly to 80° or 85° and the oxidation is complete in one or two minutes. A little bromine is set free, and the final color is orange instead of clear yellow. With the proportion of acid specified the reaction takes place smoothly, no bromine being formed. For appreciably larger quantities of hydroquinone the initial heating need not be so high; a temperature of 50° will suffice.

[1] "Organic syntheses," Collective Volume 1, John Wiley & Sons, Inc., New York City, 1932, p. 469.

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ABSTRACTS

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KEEPING UP WITH CHEMISTRY

A transparent buret reader. B. Stone. *Chemist-Analyst*, **26**, 45 (Apr., 1937).—A convenient reading device may be made from the cellophane wrapper from a cigarette package. A piece about two by two and a half inches is cut, and two parallel slits are made in the center about an inch apart and one and a half inches long. A heavy dark line about an eighth of an inch wide is drawn between the slits and parallel with them, using a glass marking or indelible pencil, moistening the cellophane if the latter is used. The reader is placed on the buret by depressing the center section. The side with the heavy line should be outermost to avoid rubbing off. With the heavy mark slightly below the meniscus, a clear, reproducible reading is obtained. D. C. L.

Paraffin treating labels. J. B. Hester. *Chemist-Analyst*, **26**, 47 (Apr., 1937).—To avoid the trouble in heating and the general messiness of trying to secure an even application of paraffin over the labels on bottles, the following offers a simple and effective remedy. Ten g. of paraffin are dissolved in one hundred cc. of gasoline or benzine. This is stored in a bottle with a small brush fastened in the stopper and is ready for immediate use. D. C. L.

The use of toluene with carbon dioxide in obtaining low temperatures. R. R. Denslow. *Chemist-Analyst*, **26**, 33 (Apr., 1937).—Toluene may be used with CO_2 to produce low temperatures in place of ether. Its melting point, −80°C., is sufficiently low for it to remain liquid, thus maintaining intimate contact with the substance to be cooled. Its low volatility makes a small amount suffice for several experiments. Less fire hazard, lower cost, and probably less offensive odor are other advantages. D. C. L.

Tannic acid in analysis. C. F. Miller. *Chemist-Analyst*, **26**, 38–9. (Apr., 1937).—Tannic acid gives reactions with many metals and radicals which are satisfactory for qualitative and quantitative purposes. It can be used to detect Ti, Fe, Cb, Ta, Ag, An, U, Hg, vanadates, molybdate, tungstates, and phosphates. Quantitatively it can be used to separate Ti from Zr, Ta from Cb, Ti and vanadates colorimetrically, and as an outside indicator in the titration of Pb with ammonium molybdate. Directions for the identifications and separations are given, with the colors of the precipitates and the sensitivity of the tests. D. C. L.

Flash curing. Anon. *Ind. Bull. of Arthur B. Little, Inc.*, **126**, 1 (July, 1937).—The vulcanization of rubber is generally accomplished by means of a definite heat treatment by which the material is heated at a closely controlled temperature for a carefully measured length of time. This "curing" of rubber is standardized. Nevertheless, this time-temperature relationship is complex and cannot be calculated reliably by mathematical methods because vulcanization involves chemical, colloidal, and physical changes which perform at differing rates with varying temperatures. The maximum temperatures employed for vulcanizing rubber were in the neighborhood of 170°C., and 163°C. was more often regarded as the practical limit of temperature of vulcanization. The undesirable secondary reactions which impair the quality of rubber were often intensified at these and higher temperatures. Contrary to this tradition of the rubber industry, the Western Electric Company and the Bell Telephone Laboratories have used temperatures above 170° and as high as 198°, effecting a cure in less than twenty seconds as against twenty minutes at 142°C. and employing a high degree of organic acceleration. The process is not applicable to all rubber vulcanization, but for the manufacture of rubber tubing, some grades of packing, thin sponge rubber sheets, rubberized fabrics, and other similar uses the process seems applicable, thus revealing a new principle in rubber technology. G. O.

C. D. alcohol. M. H. Haertel. *Chem. Industries*, **40**, 241–4 (Mar., 1937).—Social considerations and government necessities combine to impose a heavy excise tax on beverage alcohol. Manufacturing operations, on the other hand, require a low-cost raw material and cannot bear even a moderate tax on industrial alcohol. The situation at present may be summarized thus.

1. While there is no such thing as a perfect denaturing formula, it is possible to make cleaning operations so expensive, complicated, and risky that the recovered alcohol will not be worth the cost involved.

2. No permanent formula can be devised. Bootleggers will always find chemists of high technical ability and low ethical standards. The government must be on the alert, and have a new formula available at all times.

3. No one denaturant can withstand all manipulations known to the bootlegger today; it is necessary to incorporate an ingredient to meet each method of attack; the formula must be tailor-made.

The application of these principles resulted in the announcement May 27, 1936, of the modification of the two existing formulas, Nos. 5-A and 10.

The first of these prescribes six ingredients, totaling 8.75 parts of denaturants per one hundred parts of ethyl alcohol; it depends on isopropanol, Pontol, and methyl isobutyl ketone. The second has five ingredients, totaling 12.5 parts of denaturants, consisting principally of Tecsol (five parts), with Pontol, isopropanol, and methyl isobutyl ketone. Treasury chemists who are thoroughly familiar with the devices of the bootlegger, believe that these formulas will resist any manipulation known today. Only experience can tell when a revision will be necessary. A. T. B.

Production of higher aldehydes. Anon. *Chem. Industries*, **40**, 263 (Mar., 1937).—Processes by which satisfactory yields of higher aldehydes can be obtained from the corresponding higher fatty acids have been developed by chemists of Armour and Company. The methods are based on the discovery that vaporized higher fatty acids will react with formaldehyde in the presence of a catalyst to give significant yields of aldehydes. Reaction is facilitated by the presence of carbon dioxide and steam in the reacting mixture, although these substances need not necessarily be present. A. T. B.

Dry ice from waste gases. Anon. *Chem. Industries*, **40**, 380 (Apr., 1937).—The continued development of the uses of dry ice during the past few years has resulted in renewed search for cheap raw material in order to meet the increasing demand for this valuable product. Waste gases from distilleries and lime kilns are the principal sources of raw material now being used for the production of liquid carbon dioxide and dry ice, since they are the lowest cost raw material available in most localities. About seventy-five per cent. of the dry ice consumed in the United States is produced from waste gases from these sources. A. T. B.

Solvents and diluents in nitrocellulose lacquers. R. M. Carter. *Chem. Industries*, **40**, 493–5 (May, 1937).—In ordinary paint the linseed oil portion of the vehicle constitutes the film-forming body. Without it there would be no continuous protective coating. Quite to the contrary, the solvents and diluents of a nitrocellulose lacquer do not appear in the final film. They merely serve to dissolve the film-forming materials—the nitrocellulose, resins, and plasticizer—conferring upon the lacquer the property of workability. A. T. B.

Sodium metasilicate. C. L. BAKER. *Chem. Industries*, **40**, 477–81 (May, 1937).—Silicates of soda constitute one of the most diversified groups of commercial chemicals. There are crystals and glasses, solids and liquids, solutions so viscous that they will hardly flow and others nearly as fluid as water; there are free-flowing powders whose particles are really liquid. This array of commercial silicates of soda can be divided into two principal groups. The first, which represent most of the commercial tonnage, are characterized by the fact that their chemical composition is partially independent of the laws of valence. For example, one widely used grade might be represented by the empirical formula $Na_2O{\cdot}3{\cdot}22\ SiO_2{\cdot}24{\cdot}21\ H_2O$. The second group represents the crystalline sodium silicates. These are true chemical compounds and have characteristic crystal habits. Of these sodium metasilicate pentahydrate ($Na_2SiO_3{\cdot}5H_2O$) is commercially the most important.

Ten years ago sodium metasilicate was a chemical curiosity. Sticky crystals with a bad habit of cementing themselves into rock-like masses were available from one or two laboratory supply houses at a dollar a pound or more, and the use of the material was confined to infrequent bits of research. Today there is available a dry, stable, and free-flowing product of high purity, selling in carload quantities at less than two and a half cents per pound. It has become a basic alkali of unusual detergent properties and widely used in laundries, textile mills, dairies, bakeries, metal fabricating plants, and in many other industries where cleanliness is important at a low cost without injury to the material being cleaned. A. T. B.

Four nines. ANON. *Ind. Bull. of Arthur D. Little, Inc.*, **125**, 1 (June, 1937).—Now that zinc is being produced 99.99 per cent. pure, it is a metal to be watched for interesting developments. Zinc as we knew it fifteen years ago is now known to be an alloy with properties quite different from the metal itself. The greatest advance in the use of "pure" zinc has so far been made in the field of die casting. Die casting finds a wide use in such fields as the automotive, household appliance, business machine, builders' hardware, and electrical appliance industries. The process of producing pure zinc is the treatment usually confined to organic liquids, namely petroleum. The zinc is vaporized and passed through rectifying columns in one of which the high boiling impurities are separated from the zinc and the other low boiling impurities are removed in another column. The pure zinc is not so readily attacked by acids and electrolytes. Over forty per cent. of the zinc produced in the United States is consumed as galvanized products. Zinc oxide, in the form of zinc dust, is consumed in large and increasing tonnage in paint. The new high-purity zinc is reported as making possible an inert zinc flake pigment with a luster similar to aluminum paint. For the production of this plate the zinc is alloyed with less than a tenth of one per cent. of manganese and ground in a ball mill. Zinc foil will be new to commerce, but this foil when rolled produces a brilliance comparable with aluminum and tin, and as many as sixteen sheets may be passed through the rolls at one time. The rolling of aluminum is usually done two sheets at a time. The new zinc foil is reported to be stronger than the lead-tin foil metal largely used in wrapping cigarettes. This zinc foil is also an alloy product. G. O.

New developments in catalysts are reported. EDITORIAL STAFF. *Chem. & Met. Eng.*, **44**, 324–5 (June, 1937).—Cobalt as a catalyst occupies a unique position. The oxide is the most efficient oxide catalyst for the oxidation of ammonia, and the oxidation of hydrocyanic acid to NO. The sulfate is the most active catalyst for the oxidation of sodium sulfite solutions and ammonium sulfite solutions.

It has been found that members of the rare earths are effective in the oxidation of benzene to phenol, of toluene to benzaldehyde and benzoic acid. Their action is attributed to the formation of definite though unstable "intermediate" compounds.

All four of the halogens are good catalysts for many reactions. The mechanism may be interpreted from either the chemical or physical viewpoint, and either the atom or molecule of the halogen may be doing the work.

Of the metal halides aluminum chloride is the most interesting. It may cause "true polymerization" or "conjunct polymerization" of olefins.

The successful application of metallic oxides as contact agents of important organic chemical transformations is undoubtedly the outstanding single development in catalysis in the past decade or two. Their high degree of selectivity and resistance to poisons are their outstanding characteristics. Their study was taken up as a result of the developments in methanol synthesis. Catalysts containing the oxides of zinc and chromium seem to have met with the most favor. J. W. H.

Chemical engineering problems in refining platinum. C. JOHNSON AND R. H. ATKINSON. *Chem. & Met. Eng.*, **44**, 371–2 (July, 1937).—Chemical engineering problems in refining platinum are of a specialized nature, with the result that experience in other fields is not very helpful. This is especially true in the wet processes. Because of the powerful acids and other reagents which are employed chemical stoneware is used instead of the standard materials of construction. The scale of operations is small, mechanical operations are reduced to a minimum, and batch processes are preferred.

The plant for the thermal decomposition of ammonium chloroplatinate and paladosammine chloride uses fused silica trays for the salts, which are slowly heated in muffle furnaces fired by gas. The fumes evolved are drawn through a Cronite tube into a sublimate box. J. W. H.

HISTORICAL AND BIOGRAPHICAL

A new alloy of high density. P. BERGSØE. *Nature*, **139**, 886 (May 22, 1937).—Bergsøe believes that the precolumbian Indians of the Esmeraldas coast in South America used to produce coherent platinum by heating it with gold up to the melting point of the gold, and alternately heating and hammering the mass as the platinum gradually became embedded in a platinum-gold eutectic. C. J. Smithells [*Nature*, **139**, 490 (1937)] has recently described a similar method of producing copper-nickel-tungsten alloys without melting the tungsten. M. E. W.

Science news a century ago. Thomas Graham at University College, London. ANON. *Nature*, **140**, 81 (July 10, 1937).—*Nature* quotes the following passage from the *Mechanics' Magazine* for July 15, 1837: "The Chemical Chair of the London University College, vacant through the lamented demise of Professor Turner, has been conferred on Mr. Graham, the Andersonian Professor of Chemistry at Glasgow. A better selection could scarcely have been made. Mr. Graham was first made favourably known to chemical philosophers by his discovery of the laws of gaseous diffusion. He established by well-devised experiments, the conformity of gases flowing through minute orifices, to the universal physical law that determines the issuing velocities of non-elastic fluids. During the last five years he has been diligently engaged in elaborate inquiries into the constitution of salts, with special reference to the functions of their watery element, and has already published some results that are considered by good judges to affect materially the higher doctrines of chemical philosophy." M. E. W.

Epilogue to the Mendeléeff centenary. F. A. P. *Nature*, **140**, 90 (July 17, 1937).—The official report of the Mendeléeff centenary congress held in Leningrad in September, 1934, has just been published in two volumes which have been carefully edited for readers both in Russia and abroad. All the speeches of the Russian scientists and their foreign guests are given both in Russian and in French or German. The volumes contain: an address by the representative of the Moscow chemical workmen on the development of the Russian chemical industry; Professor Nametkin's lecture on Mendeléeff's services to the petroleum industry; many glimpses of Mendeléeff's unconventional personality; and some rare illustrations which are little known outside of Russia. The names of all the speakers and their subjects were given in *Nature*, **134**, 799 (1934). M. E. W.

The "Black Chamber" of 1776. F. THONE. *Sci. News Letter*, **32**, 6–7, 14 (July 3, 1937).—Secret writing during the revolutionary war is not as difficult to decipher as that of modern times. Four letters, three to John Jay and one written by him, have had their mysteries revealed by the aid of ultra-violet and infra-red rays and the camera. "Sympathetic ink" used in those letters was tannic acid which was developed by application of ferrous sulfate. No chemical developing was used in restoring the letters described in this article. B. C. H.

TEACHING OBJECTIVES, METHODS, AND SUGGESTIONS

Teaching an abstract concept in science by means of the motion picture. C. L. GUTZEIT. *Educ. Screen*, **16**, 147–8, 150 (May, 1937).—The vocabulary of the structure of matter is evident in the news of the day so its study may no longer be relegated solely to the training of the specialist in that field. Such concepts must be introduced to pupils as early as possible. It is suggested that the major teaching problem is that of finding a way whereby accurate mental imagery of three dimensions and of motion of structural units may be achieved. The motion picture is proposed as a means of attaining those two objectives which are quite generally recognized as inadequately cared for by purely verbal description. Class teaching experiments were set up, using film and non-film presentations. The films used were: Erpi Picture "Molecular Theory of Matter" and General Electric "Beyond the Microscope." Effectiveness of the teaching procedures was investigated by use of tests. While there seems to be evidence of superiority of the film method over the other, that conclusion is not supported fully by each type of the tests used. Results do indicate that the eighth grade is not the lowest perception limit for such concepts presented by the films method. B. C. H.

FOREIGN CHEMICAL AND EDUCATIONAL CONDITIONS

Recent development in Canadian chemical industries. F. G. GREEN, W. H. DEBLOIS, AND G. S. WHITBY. *Chem. & Met. Eng.*, **44**, 308–10 (June, 1937).—Canada has made notable progress in building up her chemical industries. At Trail, B. C., huge plants have been built with a daily capacity of 475 tons of lead, 400 tons of zinc, 60 tons of copper, 25,000 oz. silver accompanying gold, antimony, bismuth, and cadmium, and 475 tons of concentrated phosphatic and nitrogenous fertilizers. These are the oldest and largest of the Canadian chemical industries as well as the largest employers of chemists and chemical engineers in the pulp and paper industry.

At Copper Cliff in 1930 a plant was erected to produce sodium bisulfate as a direct product. It is used to separate nickel and copper. Several plants are now engaged in mining and dehydrating the sodium sulfate in the dried up lakes of western Canada.

Other plants have been erected within the last few years to make anhydrous synthetic ammonia, sulfur dichloride, ferric chloride, acetic acid, acetone, acetic anhydride, selenium, a wide range of refractories, an alkali-resistant Portland Cement, and hydrogen peroxide.

Within the past decade those following the professions of chemistry and chemical engineering have increased more than any professional class. J. W. H.

GENERAL

Deflating the inch. ANON. *Ind. Bull. of Arthur D. Little, Inc.*, **126**, 2 (July, 1937).—It may seem strange that one hundred and fifty years after the founding of the Republic, legislative action should be necessary to fix the value of the inch and the pound with which we are so familiar. The reason is that we have never had a statute which defines the way in which these units shall be determined. In the Constitution it is provided that Congress shall have the authority to fix the status of weights and measures. The proposal calls for the establishment of the U. S. inch as equal to exactly 25.4 millimeters which has been adopted as standard for industrial purposes by standardizing groups in fifteen countries including the United States and Great Britain. This reduction of only two parts in a million of the inch will not affect industry. Only in the most precise measurements of length as in the making and certifying of precision gage blocks and line standards of length will this proposed change be of any significance. G. O.

New beauty. F. THONE. *Sci. News Letter*, **31**, 330–1 (May 22, 1937).—Practical uses of the X-ray in the hands of the scientist have been quite widely publicized. Its potentialities in the hands of the artist have received scant attention. The gist of Dr. Thone's theme is that there is beauty below the skin of things. To reveal this inner beauty in a manner acceptable to the artist requires a technic quite different from that where the composition of the picture can be planned by the naked eye before exposure is made. In this art, instead of infra-red and ultra-violet the artists must know the effects of "hard" and "soft" rays; but time of exposure still has to be considered. In this art the worker must appreciate that the third dimension does not enter, but instead the results are more in the nature of silhouettes. The most successful outcomes, so far, have been achieved with plants and flowers. B. C. H.

Pitfalls in the rocky road of research. C. F. KETTERING. *Chem. Industries*, **40**, 257–61 (Mar., 1937).—Research is one of those things which is talked about more and understood less than any other industrial relationship. It is something which is begun too late if you don't undertake it until you have to. It is just as though you waited to see the smoke rolling out of a building before calling a fire insurance agent. You have to pay the premiums on insurance for a long time and really hope that you will never need it.

Getting an understanding between the research organization and the accountant in an industry is the most fundamental thing to do if you are going to have peace and quiet and get something done. If the research man is told by the management that he must come under the same rules and regulations regarding the financing of his operations as the rest of the concern, then the only thing for him to do is to take the most easy and obvious problems so that he can meet the forecasts and prices. But if you don't have to do that, then you can go to work and do something worth while. Then you can pick some long-range problem.

By observation, a failure may sometimes be turned into success through discoveries made in some other field. So you want to be very careful when setting up an experiment, for it's probably going to work out in a different way than you think it will. If you are keen enough on answering why an experiment doesn't work when it fails and follow that through, that is worth more than the experiment itself. Therefore, see the thing through with a lot of patience; otherwise you miss.

The only reason you try an experiment is to cultivate your own thinking. You set up an experiment and it doesn't work. That means you weren't thinking straight. You say the experiment failed. That is just your alibi. That was not it at all—it was your own thinking that failed, not the experiment.

So the experiment that fails is simply an experiment in which you were wrong. Now if you don't find out why you were wrong, your next experiment is going to be worse than the first. Remember that an experiment is an impartial judge of your thinking. You may get all fussed up and use bad words. But you made the experiment, so why should you call yourself bad names? Very few problems will permit of a thoroughly logical analysis. Most of the things that are difficult are not that logical. Consequently you must use whatever method you can use, such as mathematics, chemistry, or anything that will produce a definite set of conditions with which you can experiment. It takes the same amount of energy to do an experiment whether it is an advanced experiment or whether it is an elementary one. Such an analysis is very, very important, for just trying one experiment after another doesn't necessarily mean that you are getting any place at all. A. T. B.

RECENT BOOKS

QUANTITATIVE ANALYSIS. *William Reiman III*, Ph.D., and *Jacob D. Neuss*, Ph.D., Rutgers University. International Chemical Series, McGraw-Hill Book Company Inc., New York City, 1937. ix + 425. 13.5 × 20 cm. $3.25.

This excellent textbook of quantitative analysis makes a particular appeal as not only new but original in its arrangement and theoretical approach. The authors in the preface describe the book so thoroughly and precisely that the best review of the work would quote the authors' comments from the preface itself.

"Every theoretical discussion in the text is located immediately before or immediately after the laboratory procedure to which it applies. This juxto-position of theory and practice makes the book less flexible and augments slightly the task of the instructor who wishes to use the book with a different order of analyses. The advantage, however, of impressing the student with the intimate relationship between theory and practice far outweighs the disadvantage."

The early introduction of the theory and technic of potentiometric measurements and the graphical interpretation of results is a distinctly original and daring innovation. Volumetric analysis is taken up first, and the physical chemical interpretation is carried out systematically through acidimetry, alkalimetry, oxidation-reduction, electrolytic precipitation, and the determination of pH.

The text is intended for use in connection with a two-semester course. The first nineteen chapters are to be studied during the first semester and the last nine chapters during the second-semester course. Organic analytical reagents are included in the second-semester procedures. Oxime and dimethyl glyoxime procedures are, in particular, specific illustrations. The complete analysis of limestone and brass including the use of platinum ware is included.

The appendix of twenty-two pages is distinctly a valuable adjunct to the text, and a five-place logarithm table is included. The text has a fine list of problems after almost every chapter. The solution of these problems demands a thorough understanding of the text material for their answers. Answers are provided in seven pages at the completion of the appendix. The text is abundantly supplied with literature references, and only the most recent and timely references are included.

The text has so much of originality in teaching methods and at the same time is so much at variance with present teaching practice that it would be unwise to offer any prediction as to the popularity it may eventually command. Probably one thing is certain; it will require a particularly enthusiastic type of teacher and corps of assistants to realize the best results from its use in connection with large classes. As the authors predict, this unusual limitation is of but minor importance as compared with the reward in results which can be expected to follow.

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DEMONSTRATIONS AND EXPERIMENTS IN GENERAL CHEMISTRY. *Albert L. Elder*, Associate Professor of Chemistry, Syracuse University. Harper and Brothers, New York City, 1937. viii + 247 pp. 89 figs. 13.9 × 21.4 cm. $2.00.

In the preface Professor Elder suggests the large groups at different educational levels to whom this book should appeal. He states, "It is hoped that high-school teachers of chemistry and general science will find many suggestions for the improvement of demonstrations. The lecture assistant, be he 'Johnny,' the brightest boy in the high-school class, a senior or a graduate assistant in the smaller college, or a lecture assistant in a large university, should find in the book material suited to his needs. Suggestions are included for those who are seeking material for 'open houses' and exhibits in chemistry.

"Teacher-training classes in science require suitable demonstration material in chemistry, and this book was written as an aid for these students."

More than two hundred lecture demonstrations are provided, organized about the major topics of general chemistry. For each demonstration there is given a list of supplies needed, a description of the procedure to be followed, and, in many cases, an illustration of the apparatus used and a brief statement of the purpose of the demonstration. More than fifty references to the original literature are cited.

While the book is serious in purpose, Professor Elder does not hesitate to relate the chemical principles demonstrated to the everyday experiences of the students, as may be seen from the following list of demonstrations: soil analysis, water analysis, air conditioning, cleaning silverware, preparation (and consumption) of pectin jelly, operation of a fire extinguisher, and the testing of batteries, soaps, cosmetics, and baking powders.

Included in the volume are tables of solubility, the metric system, atomic weights, and the periodic table. The book is attractively made up, the illustrations showing unusual originality and skill.

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STRUCTURE OF ATOMIC NUCLEI AND NUCLEAR TRANSFORMATIONS. *G. Gamow*, George Washington University. A second edition of CONSTITUTION OF ATOMIC NUCLEI AND RADIOACTIVITY, Oxford University Press, London and New York, 1937. xii + 270 pp. 70 figs. + 3 plates. 16 × 23.5 cm. $6.00.

This volume presents and discusses current theories concerning the composition and structure of atomic nuclei in the light of the experimental discoveries of the early thirties. A humanly sympathetic note is struck by the plaintive comment: "whereas in writing the first edition the author felt unhappy because there were not enough experimental facts and theoretical calculations, he now feels that there are perhaps too many." The discovery of the neutron, the deuteron, the positive electron, artificial radioactivity and disintegration by neutron and deuteron bombardment have all been accomplished since 1930, when the first edition was issued. The mere recital of this list of major discoveries emphasizes not only the tremendous rate of advance but also the complete revision in theoretical concepts that was necessitated, since, as the author states, "the first requisite for a theory of nuclear structure is a knowledge of the elementary constituent parts from which the nuclei of the different elements are built up."

Topics discussed include: elementary particles and constituent parts of nuclei, nuclear binding energies and stability limits, spins and magnetic moments of nuclei, nuclear transformations —spontaneous and by collision—and a brief section on the abundance and origin of the elements. The theories of Fermi, Heisenberg, Majorana, and Gamow are considered in detail. A number of valuable tables, *e. g.*, of masses and relative percentages of nuclei of stable isotopes, of mechanical and magnetic moments of nuclei, of unstable elements and their transformations, of nuclear reaction, etc., are included.

Barely sufficient experimental data are included to supply background information concerning nuclear properties and reactions to serve as a basis for theoretical consideration. The theoretical discussions are presented in concise and lucid English and conclusions are drawn with beautiful precision. Of approxi-

mately two hundred citations to the original literature somewhat over twenty are to publications by the author. This indicates the extent of the author's own important contributions, but a partial explanation might also be derived from this delightful comment encountered at the close of a discussion of nuclear shells. "One may hope that further investigation along these lines will add considerably to our understanding of more detailed problems of structure. Much has already been done, with rather overlapping results by Bartlett, Gapon, Ivanenko, Elsasser, Guggenheim, and others; it is not referred to in detail here [nor are any literature citations made at this point] because the author was never able in studying these articles to remember the beginning when he was reading the end!"

Other excerpts of interest include, "Widespread experimental research into different types of artificial nuclear transformation has brought this part of nuclear physics to a stage almost comparable with that of our present knowledge of molecular reactions. . . . .

"It appears that future theory must give up the description of the electron as a particle in favour of some other description which may well differ in point of view from Dirac's present theory as radically as the modern wave mechanics differs from the old postulates of Bohr. . . . .

"Introducing neutrons as nuclear constituents [in 1932] it became possible to eliminate the two main difficulties [electron behavior within atomic nuclei and discontinuities in nuclear binding energies] which the earlier model encountered. . . . .

"The question has frequently been raised whether the neutron should be considered as a complex particle, built up from a proton and an electron, or a proton regarded as formed from a neutron and a positron, . . . it seems very likely already that the question 'which of these two particles is the simple one?' has no physical meaning. Rather, neutrons and protons should be considered merely as two different states of the 'fundamental heavy particle,' subject to transformations from one to the other with the emission or absorption of energy and the liberation of (negative or positive) charge. . . . .

"The number of protons with which a given neutron can interact and vice versa (the number of possible valency-bindings between these two particles) depends on the special assumptions concerning the type of exchange which takes place between these two particles. [At least to a mathematical physicist.] In his original hypothesis Heisenberg assumed (by analogy with molecular interactions) that only the exchange of electric charge takes place between neutrons and protons which leads to a single valency between these two particles. This hypothesis was modified by Majorana who supposed that both charge and spin of the particles are exchanged in which case one obtains a double valency, each neutron being able to bind two protons and vice versa... The experimental fact that alpha particles and not deuterons possess an exceptionally high stability speaks definitely in favour of Majorana's type of exchange. . . . .

"That many more negative electrons than positive electrons are observed in our common experience. . . may now be regarded as merely the local peculiarity of the part of the universe in which we are living. . . . .

"The negative proton is to be regarded—if its existence be assumed—merely as an independent particle subject to intertransformation with a neutron involving the emission of an electron or a positron, as the case may be . . . An interesting consequence of the introduction of negative protons as nuclear units is the possibility of constructing isomeric nuclei, with both atomic number and mass number the same for each, differing one from the other in the matter of internal structure only [*i. e.*, isomeric isobaric, isotopes; *e. g.*, UX_1] . . . As far as present knowledge goes there occur 48 isobaric pairs and 3 isobaric triplets among the 'stable' nuclei with mass numbers 1 to 209. . . .

"Even the simple study of the relative numbers of neutrons and protons in different nuclei allows us to reach rather interesting conclusions concerning nuclear structure and at the same time permits us to explain certain anomalies of behaviour which must almost certainly be connected with the completion of saturated shells in the nucleus at various stages in its synthesis. . . .

"The process of β-disintegration has, until quite recently, offered serious difficulties to theoretical understanding. . . we have the choice only between two possibilities: *either, as proposed by Bohr, the energy-conservation law does not hold for the processes of β-disintegration, or, according to the hypothesis of Pauli, energy is taken away by some new kind of particle still escaping observation* [the neutrino] . . . . This particle can have no charge (as all the charge is already taken by the electron) and its mass must be small compared with that of the proton (as the mass number does not change in β-disintegration). These two properties alone make this hypothetical particle, now called the *neutrino*, extremely difficult to observe . . . . Experiments in this direction have been undertaken by Lejpunskij . . . . the results of these experiments seem to be in favour of the existence of the neutrino . . . .

"Nuclear electrons are never observed to be *ejected* immediately in the process of collision; . . . such emission when it occurs . . . always takes some time which is characteristic of the nucleus itself having nothing to do with the nuclear reaction in which the β-emitting nucleus is produced . . . .

"The naïve description of a substitutional reaction would consist in the hypothesis that the incident particle, upon entering the nucleus, gives its energy by direct collision to some other particle previously existing in the nucleus, thus throwing it out. However, it seems that such a simple picture cannot correspond to reality, as, for example, if the ejected particle is an alpha particle it seems doubtful whether we can treat it as 'existing' in the nucleus before the transformation . . . .

"It was later shown by Fermi and his collaborators that practically all elements, especially heavy ones, being bombarded with neutrons capture the incident neutrons, thus forming the heavier isotope, and emit the surplus energy in the form of gamma radiation . . . .

"The investigations of Aston have shown that the relative amounts of the different isotopes of a given element remain very nearly constant for samples obtained from very different places on the earth's crust. This is probably also true on the astronomical scale, as, for example, the ratio of the amounts of the lithium isotopes Li^6 and Li^7 in the chromosphere of the sun (determined by a spectroscopic method) is exactly the same as the corresponding ratio for the ordinary lithium used in our laboratories . . . . "

The publishers state that the author "gives a full account of theory and experiment on the nucleus up-to-date, including all the new facts and theories, but omitting any elaborate mathematics." This is not to be interpreted to mean that the elementary algebra and calculus to which the chemist all too frequently confines himself is adquate; a knowledge of at least elementary quantum mechanical methods is necessary.

This is a valuable addition to the literature of the nuclei. It should prove very useful for graduate students, particularly for use in courses or seminars on radioactivity or nuclear structure. These can hardly fail to recognize the debt they owe one with the courage and diligence to undertake such a survey of this, so rapidly changing, field.

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ERIE CENTER
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ATOMIC STRUCTURE OF MINERALS. *W. L. Bragg*, The Victoria University of Manchester, Manchester, England. Cornell University Press, Ithaca, New York, 1937. ix + 292 pp. 144 figs. 15 × 23 cm. $3.75.

This book is a record of Professor Bragg's lectures at Cornell University as Baker Non-Resident Professor in 1934. It is intended primarily for mineralogists, crystallographers, and crystal analysts. Minerals are listed according to their general chemical types, and for each type the crystal structure of the various minerals is given in considerable detail. Considerable stress is put upon the relations between the structures of chemically similar types, and isomorphous substitutions (variate atom-equipoints) are considered to be the rule, rather than the exception, in min-

erals. The structures are amply illustrated by figures so drawn as to assist the reader in building models of the various minerals for himself.

The first three chapters contain a summary of crystal lattices, point-groups, and space-groups, (sixteen pages); a review (twelve pages) of the methods of crystal analysis; and nine pages on ionic sizes, coördination numbers, Pauling's principle, and variate atom equipoints. These thirty-seven introductory pages serve to give all readers a common starting point by outlining for them, from the standpoint of the author, subject matter which they are assumed to know already.

The book is written in that particularly clear style which has already become associated with the name of Bragg. It will prove of real value as a reference book on structural and chemical mineralogy. The late date of publication has enabled Professor Bragg to include all important work in the literature up to the end of 1936. The book should be in the library of every crystallographer, mineralogist, ceramist, and crystal analyst.

WHEELER P. DAVEY

SCHOOL OF CHEMISTRY AND PHYSICS
THE PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PENNSYLVANIA

ORGANIC CHEMISTRY LABORATORY GUIDE. *E. Wertheim*, Ph.D., Professor of Organic Chemistry in the University of Arkansas. P. Blakiston's Son and Co., Inc., Philadelphia, 1937. xxii + 524 pp. 21.5 × 28 cm. $2.00.

ORGANIC CHEMISTRY LABORATORY GUIDE "presents experimental material for a year's course in elementary organic chemistry," and is "especially designed for those students who are majoring in chemistry and those following the engineering or premedical curriculum." In addition to the more or less standard preparations, a few experiments are included that are not given in the usual manual and some of the preparations approach the semimicro procedures. Adequate test-tube experiments and identification reactions are included. Each experiment has a time schedule which should serve to stimulate the student to improve his laboratory dexterity. Mechanically, the manual presents a very good appearance.

Only standard apparatus is required, and detailed instructions are given for carrying out the procedures. "All of the experiments have been tried by the author and a great effort made to avoid errors." Removable report sheets for all of the experiments, two hundred eighteen pages, are included as a part of the LABORATORY GUIDE. A space is provided in each report for the instructor's approval before the student proceeds with the assignment. The questions on the report sheets aim to "test the student's knowledge of what he has done and show him the relationship of the compounds he has worked with to others."

The first eleven experiments are devoted to important technic exercises, forty experiments deal exclusively with test-tube exercises (a number of the preparations include some test-tube exercises), and six experiments aim to familiarize the student with the basic concepts of the identification of organic compounds. One hundred forty-five experiments are included.

Preparations are given for methane, ethane, ethylene, acetylene, ethyl bromide, methyl iodide, iodoform, tertiary butyl chloride, ethylene bromide, ethyldimethylcarbinol, diethyl ether, chloral, acetone, glacial acetic acid, formic acid, acetyl chloride, acetic anhydride, ethyl acetate, amyl nitrite, orthoformic ethyl ester, a sodium soap, acetamide, trichloroacetic acid, oxalic acid, succinic anhydride, methyl hydrogen succinnate, acetonitrile, methyl amine, benzene, *p*-xylene, ethylbenzene, diphenylmethane, bromobenzene, *p*-dibromobenzene, nitrobenzene, hydrazobenzene, *m*-dinitrobenzene, *p*-nitrochlorobenzene, aniline, *p*-bromodimethylaniline, tetrabromodiphenylamine, 5-iodo-2-toluidine, *m*-nitroaniline, *p*-nitroacetanilide, *p*-nitroaniline, diazoaminobenzene, aminoazobenzene, iodobenzene, chlorobenzene, *o*-chlorobenzoic acid, benzyl alcohol, triphenyl carbinol, phenol, *p*- and *o*-nitrophenol, picric acid, phenetole, Nerolin, β-naphthyl acetate, *o*-phenetyl urea, *p*-phenetyl urea, benzoic acid, *p*-nitrobenzoic acid, benzamide, benzonitrile, methyl benzoate, aspirin, *o*-phenoxybenzoic acid, benzoin, benzil, benzilic acid, benzalaniline, salicylic aldehyde, *p*-hydroxybenzaldehyde, acetophenone, anthraquinone, anthrone, phthalimide, anthranilic acid, phenylglycine-*o*-carboxylic acid, indigo, methyl orange, helianthin, Orange II, Martius yellow, and xanthone. Alternate procedures are given for acetone, aniline, iodobenzene, *p*- and *o*-nitrophenol, benzoic acid, benzamide, and anthraquinone. Some test-tube preparations are included.

The reviewer has only two criticisms of the manual: namely, the fill-in type of report, and the suggestive type of question to be found in some of the exercises. The student should, *in the opinion of the reviewer*, be taught to write an adequate report, and to use his senses in such a way that he will be able to feel, to see, or to smell the indications of the reaction without being forewarned.

ED. F. DEGERING

PURDUE UNIVERSITY
LAFAYETTE, INDIANA

MOTION PICTURES OF THE WORLD, The Educational Film Directory. International Educational Pictures, Inc., 40 Mount Vernon Street, Boston, Massachusetts. 66 pp. 27.5 × 21.5 cm. Subscription price $2.00, each additional year or subscription $1.00. (Four issues annually.)

"The first issue of the new MOTION PICTURES OF THE WORLD will be published toward the end of September. This will be devoted to arts and sciences. The second issue, to be published about the end of November, will be arranged by countries. The third and fourth issues, to be published each spring, will be completely revised editions of the first two issues. There will be no supplements."

For the convenience of subscribers pending issuance of the new quarterly the current issue of the clearing-house directory will be supplied free of charge. This notice supersedes any which have appeared earlier.

BEARING METALS AND ALLOYS. *H. N. Bassett*, Chief Chemist, Egyptian State Railways. Edward Arnold and Company, London. 1937. xiv + 428 pp. 30 figs. 123 tables. 15 × 22 cm. $8.50.

In the foreword of this book Sir Henry Fowler points out that of the so-called minor points of engineering none is of more importance than the bearing. In spite of the growth of roller and ball bearings, there are still many applications of plain bearings. This book is the outgrowth of a card index kept by the author for many years covering the whole field of bearing metals. It has as its purpose the summarizing of as much information as possible on this subject for the works engineer and for the designer of machinery. Enough of the modern theory of alloys is included to point the way to research, but the book is definitely written for practical use. It does not arbitrarily state which bearing metals must be used in individual cases, but gives information upon which the engineer can work. The metals include the "white-metals," copper alloys, zinc, lead, and phosphor bronzes and miscellaneous bearing metals. Some space is devoted to the subject of lubrication. There are abundant references to books and journals. The tables outnumber figures, but the latter are very clear and are mainly photomicrographs.

While this book is written primarily for experienced mechanical engineers and metallurgists, it has a place in the libraries of engineering schools. For the chemist in the small plant who has to do some engineering work and for the chemical engineer who often has to qualify as a mechanical engineer, this book is very valuable as a reference text.

W. T. READ

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TRADE ANNOUNCEMENTS

Microscope Polarizing Attachment

In recent years micro-chemistry has developed into a prominent field of chemical analysis. Much of this work has been done in private laboratories and in educational institutions where expensive apparatus was available. Schools with limited apparatus are handicapped because polarizing microscopes are not available for the examination of the many chemical compounds, both organic and inorganic, which crystallize in such form that valuable data, unavailable through other means, is made visible in polarized light.

Although the polarizing microscope can be used only on transparent crystals this is no disadvantage since almost all crystals, except those of the metals, are transparent when in a sufficiently thin section. Transparent crystalline substances possess characteristic optical properties which distinguish them from other similar substances, and in chemical analysis, when the field of inquiry has been narrowed down, final determination of a crystalline compound can be arrived at through a study of such optical characteristics. In other cases, examination through the polarizing microscope serves to provide a short cut as against ordinary analytical and physical methods. For example, the polarizing microscope can be used to identify the constituents of salt mixtures, while the chemical analysis of them gives only the ions present.

The availability of an inexpensive microscope polarizing attachment, such as that made by the *Polarizing Instrument Company* of New York City, makes it possible for schools with limited budgets to convert all microscopes now in their laboratories into polarizing equipment.

"Condenser News"

The Scientific Glass Apparatus Company of Bloomfield, New Jersey, is now publishing a house organ called "Condenser News." This booklet will illustrate and describe new products for the chemical laboratory. Chemists interested in receiving this publication periodically are requested to write for their copy.

New Stable Solution of Oxyquinone Derivatives Developed

The Ba-Re Company, 185 Madison Avenue, New York City, is producing a new stable solution of oxyquinone derivatives. It is generally known that the most interesting group in organic chemistry are the quinone derivatives. S. J. Kochor's recent investigations of these derivatives enabled him to produce the new solution. This solution has an extreme sensitivity toward cations, particularly toward barium ions. The rapid and accurate volumetric sulfate determination described by S. J. Kochor [*Ind. Eng. Chem., Anal. Ed.*, 9, 331 (1937)] is based on the fact that a few ten-millionths of a gram of barium ions will produce on test paper (treated with stable oxyquinone solution) distinct rose-red colored precipitate. The excess of barium ions added to a sulfate solution can be retitrated with standard sulfate solution to negative spot test, which is taken as endpoint. From submitted experimental evidences it is to be expected that this simple volumetric method in a short time will be accepted by the analytical chemist.

Photoelectrically Balanced Potentiometer

The *C. J. Tagliabue Manufacturing Company* has just announced a new recorder called the "Celectray." In this radically new type of recorder, a sensitive mirror galvanometer is the primary controlling element in which an inertialess beam of light takes the place of the customary metal boom or pointer. The beam of light from the galvanometer in moving on and off a phototube passes the "controlling edge" of a screen, thus operating relays which in turn control a reversing motor which drives the moving contact of the Wheatstone bridge or potentiometer. The phototube is not a calibrated element but serves only to detect the direction of the light-beam and bring the galvanometer to zero deflection, according to the well-known null method of balancing an electric circuit. The new instrument, therefore, is not a "photoelectric potentiometer" in the sense that a balance of photoelectric current is implied.

It is evident that the galvanometer is free at all times from mechanical engagement, and this fact, together with its low moment of inertia, permits rapid balancing and control actions. Furthermore, a high current sensitivity is available, permitting the use of high resistance, or of very long thermocouple leads without material loss of accuracy in the balancing. Or, on occasion, a very low scale range does not require the use of a very low resistance and its resultant disadvantages.

It is claimed that the new instrument is noteworthy for its extreme simplicity, accuracy, and speed, particularly in the multiple point recorders.

Ful-Control Laboratory Heater

Supplementing its present line of laboratory heaters and hot plates, the *Precision Scientific Company, 1736–54 N. Springfield Avenue, Chicago,* announces their new Ful-Kontrol Laboratory Heater, which adjusts from 0 to 750 watts, for mild or intense heating.

Throughout the full range of heat control, variation is virtually stepless, actually running up the scale in increments of less than one volt.

The secret is a built-in auto-transformer instead of a conventional rheostat. Not only does the heat control cover a wide range, but heat dissipation is reduced, as a characteristic of the auto-transformer.

The development of this item is of unusual significance to laboratory workers because it represents a radical departure from the usual apparatus-builder's practice of restricting its usefulness by designing it only for a single application. The Ful-Kontrol Heater, unlike its predecessors, is offered with any one of several interchangeable tops, at no extra cost, and accommodates several useful accessories, all listed in Bulletin TS 1600.

Automotive Pyralux

A new automotive finish to be known as Automotive Pyralux is announced by *E. I. du Pont de Nemours & Company.* Designed chiefly for touching up synthetic resin finishes and for recoloring used cars, it combines the quick-drying qualities of lacquers and the luster of synthetic resin enamels, requiring no rubbing. Its chalking resistance is comparable to that of baking enamel. The new finish is offered in black and twenty-six shades.

Catalog of Technical Books

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